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Characterization of Boron Films Prepared by Chemical Vapor Deposition and their Applications in X-Ray Imaging

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Characterization of Boron Films Prepared by Chemical Vapor Deposition and their Application in X-ray Imaging

ABSTRACT

Boron, a low Z element, is useful for x-ray optics since it has a low atomic absorption coefficient. Boron films prepared by chemical vapor deposition were characterized optically, electronically and mechanically. Auger, infrared and hydrogen effusion analyses showed that the films are amorphous hydrogenated boron. The hydrogen content ranges from 8% to 71%. The measurements of the complex refractive index and the resistance vs. temperature determined that they are a typical amorphous semiconductor with the energy gap ranging from 1.09 eV to 1.36 eV, decreasing with increasing hydrogen content and the Fermi energy level is pinned about midgap. The real refractive index at 490 nm increases from 3.25 to 3.59 with increasing hydrogen content. The Young's modulus and hardness were found to be 3.05×10^{13} dyne/cm² and around 2500 Vickers, respectively. A method of measuring optical index of boron films is proposed and described, as well as a model that determines their Young's modulus and predicts the bending of the boron/silicon structure. The chemical tests suggested that boron films are stable in nonoxidizing bases and concentrated acids. Some oxidizing bases such as a basic ferricyanide solution are good etchants for CVD boron films. Boron coating on beryllium windows as a corrosion barrier layer and self-supporting boron windows are set forth as potential products of x-ray imaging.

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I. INTRODUCTION:

Why Study CVD Boron

As is well known, the atomic absorption coefficient, σ_a , is equal to the linear absorption coefficient divided by the number of atoms per unit length and per unit cross section of an x-ray beam. This coefficient is given by an empirical formula relating the atomic number of the absorbing material and the wavelength of the incident light^{1,2,3}:

$$\sigma_a = CZ^4\lambda^3 + B,$$

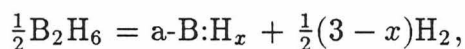
where Z is the atomic number, λ is the wavelength, C and B are constants. B can be negligible except for the lightest elements and wavelengths $< \sim 10^{-10}$ m.

Therefore elements with low atomic number, Z , are useful for soft x-ray optics since they have low atomic absorption coefficients. Beryllium, a low Z element, is often used because it is strong, tough and has a low absorption coefficient for soft x-rays. It is toxic and is chemically active and thus has considerable limitations in manufacturing soft x-ray devices. Lithium, one of the low Z elements, is even more chemically active. The rest of the elements of that row in the periodic table are gases except for boron and carbon. Boron, thus, a chemical element with the next lowest atomic number to beryllium, merits scientific investigation for x-ray application.

There have been some reports on the properties of amorphous boron. Most of the papers, however, dealt with the chemical properties of bulk crystal or

polycrystalline boron and boron compounds^{4,5,6}. Only a few papers are concerned with boron films. H. O. Pierson⁷ published a paper on depositing boron thin films via cold wall chemical vapor deposition (CVD), but he did not characterize the boron films. N. A. Blum et al.⁸ discussed the infrared absorption of amorphous boron film prepared by evaporation. Nobuyoshi Morita and Akira Yamamoto⁹ presented a paper on the optical and electrical properties of bulk boron and evaporated boron films. Koun Shirai and Shun-ichi Gonda¹⁰ published a paper on the characterization of hydrogenated amorphous boron films prepared by cyclotron resonance plasma chemical vapor deposition method. No paper, however, has been published on the characterization of low pressure hot wall CVD boron films. This technique, low pressure hot wall CVD, is well suited to the large scale deposition of thin films.

We built a hot wall CVD system (see Fig. 1.1) involving the following chemical reaction to deposit boron thin films:



where a-B:H indicates amorphous boron containing a certain amount of hydrogen, B_2H_6 is diborane. It is found that the system works well.

My dissertation treats the characterization of hot wall CVD boron and its potential value in x-ray optical systems.

In Chapter II the deposition conditions for CVD boron are discussed. Chapter III focuses on the determination of the structure and composition of CVD

a-B:H film by Auger analysis, infrared spectra and hydrogen effusion test. In Chapter IV a method to measure the refractive index for amorphous boron thin films is described. From the measured transmission and the refractive indices the energy gap of the CVD a-B:H film can be found. Chapter V covers the measurement of a-B:H resistance versus the temperature. The electrical activation energy of the low temperature CVD boron can be found from these measurements. In Chapter VI a formula is derived to determine the stress and Young's modulus of the boron films. Chapter VII shows the results of tests made for the CVD boron films, as well as beryllium foils, to indicate how they can resist caustic environments and what is a good etchant for them. A brief description of potential applications of the amorphous boron films in x-ray imaging is given in Chapter VIII. The last chapter is a summary and points out areas of research which could probably be studied.

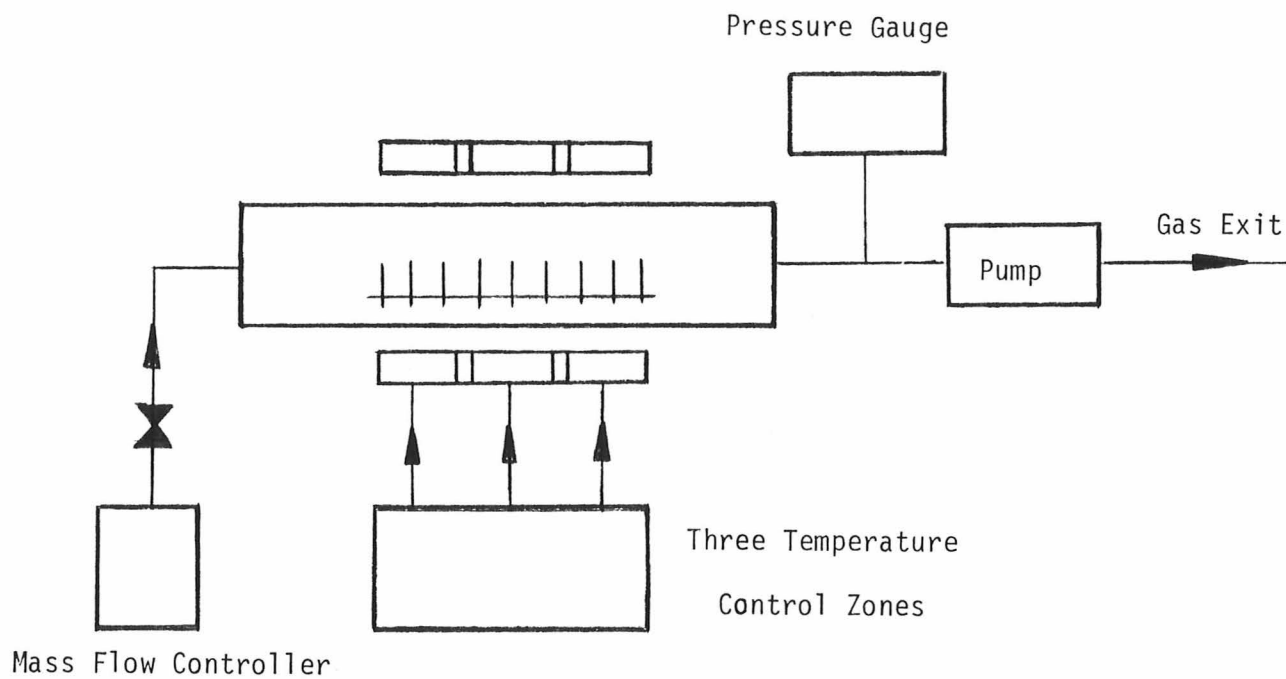


Fig. 1.1 Schematic diagram of the CVD system.

II. DEPOSITION CONDITIONS

FOR CVD BORON

Chemical vapor deposition is the formation of a non-volatile solid film on a substrate by the reaction of vapor phase chemicals (reactants) that contain the required constituents. The reactant gases are introduced into a reaction chamber and are decomposed or reacted at a heated surface to form the thin film. So the key question is what are the proper gas sources and proper temperature for a certain chemical reaction.

From the plot of free energy difference before and after the chemical reaction versus temperature of the reaction¹¹, we can find that for one mole of hydrogen H_2 , the free energy difference, ΔG_f , i.e. $G_{fB} + G_{fH_2} - G_{fB_2H_6}$, is negative and becomes lower and lower as the temperature goes higher and higher. This means that in principle diborane should dissociate more readily as the temperature goes higher.

However the barrier to reaction is kinetic, not thermodynamic. The reason that diborane does not dissociate at ambient conditions is that there is a kinetic barrier. According to Pierson's paper⁷, 400°C is sufficient from the viewpoint of chemical kinetics to overcome the chemical barrier. We chose 450°C as a nominal reaction temperature for our process. Fig. 2.1 shows the temperature distribution inside the chamber.

As we know, the surface reaction, in general, can be modeled by a thermally

activated phenomenon which proceeds at a rate R , given by¹²:

$$R = R_0 e^{-[E_a/kT]},$$

Where R_0 is the frequency factor, E_a is the activation energy in eV, and T is temperature in °K. According to this equation the surface reaction rate increases with increasing temperature. For a given surface reaction the temperature may rise so high that the reaction cannot proceed at the rate at which reactant species arrive at the surface. In such cases the reaction cannot proceed any more rapidly than the rate at which reactant gases are supplied to the substrate by mass transport, no matter how high the temperature is increased. This situation is referred to as a mass-transport limited deposition process. On the other hand, at lower temperature, the surface reaction rate decreases, and eventually the arrival rate of reactants exceeds the rate at which they are consumed by the surface reaction process. Under such conditions the deposition rate is reaction rate limited. In actual processes the temperature at which the deposition condition moves from one of the growth regimes to the other is dependent on the activation energy of the reaction, and the gas flow conditions in the reactor.

Under the low pressure of a CVD (LPCVD) reactor (~ 1 torr) the diffusivity of the gas species is increased by a factor of 1000 over that at atmospheric pressure¹². Thus there is more than an order of magnitude increase in the transport of reactants to the substrate surface, and the rate limiting step is thus

the surface reaction.

It is found that there is little dissociation of diborane at lower than 350°C. At nominal temperature of 450°C, the LPCVD deposition zone is 5 inches long with 50 sccm input gas. This shows that the reaction rate is in the reaction rate limited regime which is well suited to large scale deposition of thin films.

Under this condition we can deposit satisfactory hydrogen containing boron films. These films turned out to be relatively smooth and have excellent adhesion to silicon substrate, up to a thickness of about 3 μm for conventional 3 inch wafers, if the surface of the silicon wafer is adequately cleaned before deposition.

Appendix 1 outlines the cleaning procedure for the silicon wafers which guarantees excellent adhesion of boron films within the film thickness mentioned above.

Temperature Profile CVD System

rt=90F, m=0, f=690, r=555, flow=2.48v

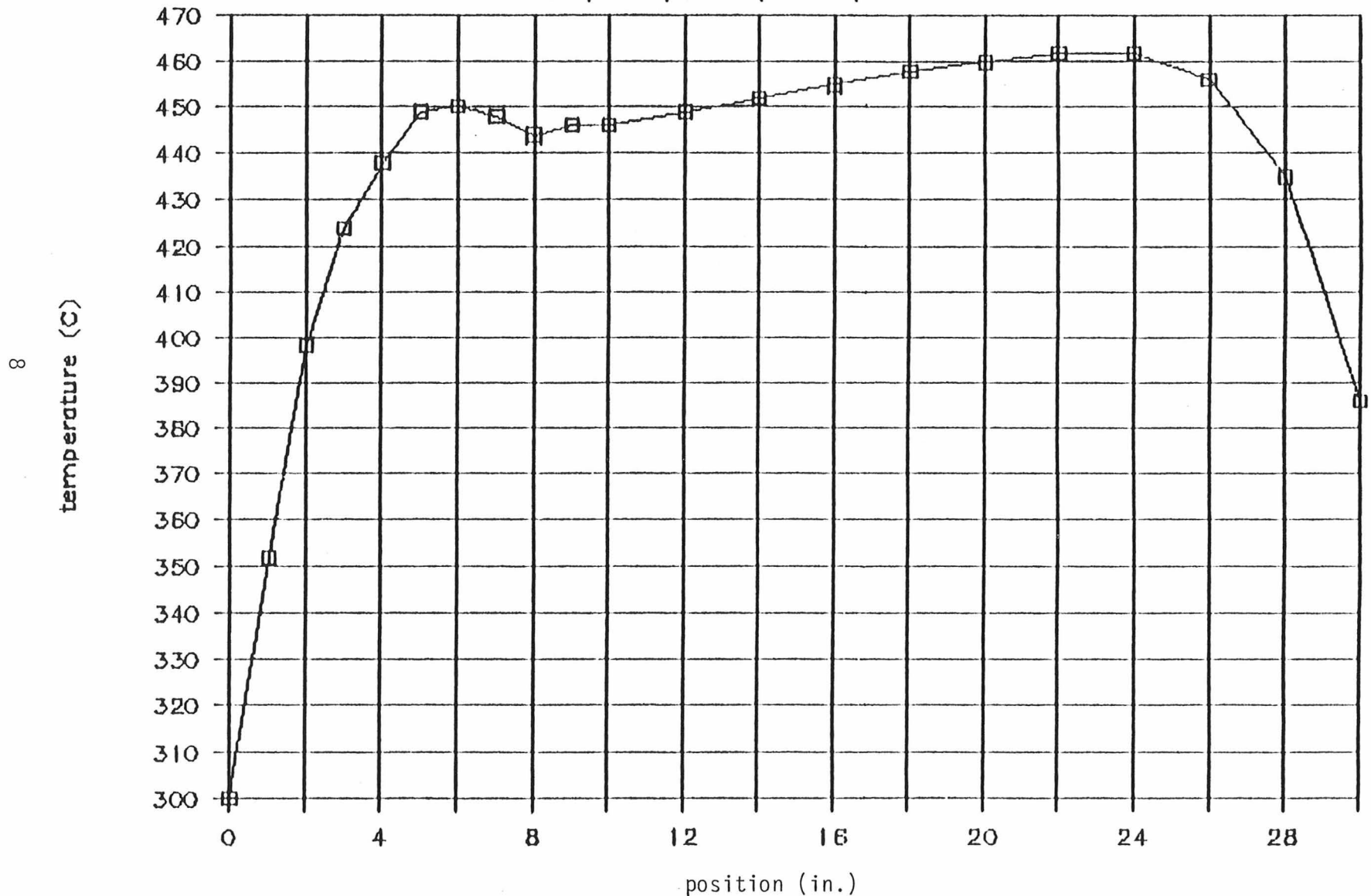


Fig. 2.1 The distribution of temperature in the tube (see the attached data)

Furnace Temperature Profile, Boron Deposition

Furnace Temp = 450C

Setting m = 50, f = 690, b = 555

Argon Flow range = 50ml/min

Furnace Temp = 450C

Posi (in)	Temp (C)
-----------	----------

0	300
1	352
2	398
3	424
4	438
5	449
6	450
7	448
8	444
9	446
10	446
12	449
14	452
16	455
18	458
20	460
22	462
24	462
26	456
28	435
30	386

III. DETERMINATION OF THE COMPOSITION AND STRUCTURE OF CVD A-B:H FILM

The first question we need to be concerned about is the structure of a CVD boron film. Is it likely to be amorphous or crystalline?

There are a lot of examples showing that CVD and evaporated deposition can produce amorphous semiconductor thin films. For example, it is reported that the evaporated boron films deposited at room temperature are amorphous^{8,9}. This could occur if the boron atoms arrived on the surface of growing films and stuck randomly at or near the place where they landed. It is also reported that by thermally decomposing silane at about 600°C amorphous silicon^{14,15,16} films can be produced. The CVD process conditions of boron films is similar to that of CVD a-silicon films. The nominal temperature we chose for boron deposition is 450°C. CVD boron films, thus, are quite possibly amorphous. To determine the structure of a sample x-ray diffractometer (XRD) and infrared spectrometer (IR) are often used. Since boron has a low atomic scattering factor¹⁷ and sample films are thin, the detector cannot receive adequate signal to determine the structure of the samples by XRD. Thus, we use IR to analyse the structure of the sample.

The second question we need to be concerned about is the composition of CVD boron film. Is it likely to be pure boron film? The gas source we used includes diborane and argon. They are each 99.99% pure. The only other element

which may possibly exist in the film is oxygen due to leaking or outgassing into the CVD system. On the other hand the system is known to have a very low leak rate and oxygen incorporated should be small.

We can expect, however, that hydrogen is included in the boron film. Hydrogen is bonded in the reactant, diborane. Incomplete pyrolysis is a well known phenomenon for films deposited from hydrides. For example, amorphous silicon films deposited by CVD from silane contains hydrogen^{14,15,16}.

The techniques for determining the composition of a sample include Auger analysis, IR and secondary ion mass spectroscopy (SIMS). Unfortunately SIMS is not available at BYU. The UNAM Laboratory in Ensenada, Mexico, however, was able to perform Auger analyses in support of this research. The data they provided can determine all the composition elements inside the CVD boron films except a few elements such as hydrogen, since Auger is a three electron effect. IR, nevertheless, can probe hydrogen qualitatively. Furthermore, nuclear reaction analysis^{18,19} (NRA) and the hydrogen effusion technique can determine hydrogen content quantitatively. Since NRA is not convenient, hydrogen effusion becomes a proper method to be applied here.

There are three sections in this chapter. Section 2.1 discusses the Auger analysis for the CVD boron film. IR experiment is described in Section 2.2. The last section discusses hydrogen determination by hydrogen effusion.

3.1 Auger Analysis

The technique of Auger emission spectroscopy^{20,21,22} involves the bombardment of a solid by an energy beam. A primary electron ejects an electron from certain shell, for example, a ground energy shell, and an electron from the above energy shell of the same atom relaxes into this shell, emitting a photon in the process. In some cases this photon escapes the material, but in others it interacts with and causes the ejection of an electron in another energy shell. Electrons ejected according to such mechanisms are called Auger electrons. The energy of the ejected Auger electrons are thus characteristic of the type of atom that emitted them. There are several such characteristic Auger transition for most elements. However, since three electrons must be involved, elements with fewer than three electrons, such as hydrogen and helium, can not emit Auger electrons.

Most Auger electron energies are between 20 and 2000 eV. The depth from which they can escape from the solid without losing a significant percentage of energy is quite shallow, generally less than 50 Å. Thus, Auger emission spectroscopy is a technique that can only provide compositional data about the surface layers of samples.

To obtain the information about the composition of the material at depths greater than the escape depth of Auger electrons the technique of ion sputtering is often used. Ion sputtering can mill through the sample gradually. Thus the Auger data can be plotted as a function of sputtering time and a depth of profile

can be obtained.

Fig. 3.1 shows the Auger data of a CVD boron film. Fig. 3.1(a) indicates that there is boron, carbon and oxygen on the surface of the film. From the plot, it is clear that the main component is boron. Fig. 3.1(b) is a plot of atomic concentration against sputtering time. This plot shows that boron is the only detectable element existing inside the CVD boron film. Due to the systematic error, when the boron atom concentration is 100% it is displayed as only about 93%. The Fig. 3.1(c), an Auger spectroscopy plot of the same sample after 120 minutes of sputtering, verifies that carbon and oxygen atoms are no longer present. The only detectable element is boron.

It is not surprise that carbon and oxygen are found on the surface of the film. Both are ubiquitous in our environment in the form of dust, oil and moisture which can be easily bound on the surface of the sample once it is exposed in the air. In addition, when the sample is exposed in the air for a long time, a very thin film of boron oxide may form. The Auger analysis tells us that neither oxygen nor carbon impurities above the level of 0.25% are incorporated within the film during the process of chemical vapor deposition. The analysis, however, cannot reveal any information about hydrogen content. The following experiments are needed to characterize the sample further.

3.2 Infrared Spectra of Amorphous Boron

3.2.1 Introduction

Infrared absorption spectra²³ are usually obtained by placing the sample in one beam of a double-beam infrared spectrophotometer and measuring the relative intensity of transmitted (and therefore absorbed) light energy versus wavelength (or wave number).

As is known, a molecule is not a rigid assemblage of atoms. A molecule can be said to resemble a quantized system of balls of varying masses, corresponding to the atoms of a molecule, and spring of varying strengths, corresponding to the chemical bonds of a molecule. Since the system is quantized only certain bond vibration frequencies are allowed. When infrared light of the correct frequency for one of the quantized mode is incident on the sample, the energy is absorbed and the amplitude of that vibration is increased. The frequency of the bond vibration will depend on the kinds of atoms and the bond structure. Therefore, IR spectroscopy provides an attractive, non-destructive procedure for qualitative structural and compositional analysis of thin films.

In Appendix 2 a table of infrared absorption of evaporated amorphous boron films containing carbon and hydrogen is given by N. A. Blum et al⁸. They indicated the following points:

- (1) The relatively narrow band at 2560 cm^{-1} observed in hydrogen doped amorphous boron samples is due to B-H bond vibrations.

(2) The broad band near 800 cm^{-1} has been observed in all samples of amorphous boron. The broad absorption regions near 1100 and 800 cm^{-1} in the amorphous samples overlay a series of narrower bands which have been observed in bulk crystalline boron samples²⁴. This phenomenon of smearing out of the fine structure in the spectra of amorphous boron samples is consistent with what one would expect in a system lacking long-range order.

Although the boron film prepared by Blum⁸ was vacuum deposited, which is different from CVD processing, the IR absorption could be expected to be similar.

3.2 Infrared Transmission Test and Discussion

Since Auger process is a three-electron effect as was mentioned above, it cannot detect hydrogen in a sample. The IR transmission test, however, can detect hydrogen if the CVD boron film contains it.

In Fig. 3.2 the spectrum of a silicon wafer with both sides polished is displayed. In Fig. 3.3 the infrared spectrum of the boron thin film coated on one side of a thin silicon wafer is displayed. Comparing these two spectra we can see that there are several absorption bands in Fig. 3.3 which do not appear in Fig. 3.1. These are solely due to the boron film.

There are three clear absorption bands in my samples. In the transmission spectrum of the sample there exists a narrow band at 2558.3 cm^{-1} which is very close to Blum's 2560 cm^{-1} . This mode is only found in hydrogen containing

samples (see the table in Appendix 2). We can, therefore, conclude that this boron film contains hydrogen.

Blum⁸ and Golikova²⁴ have concluded that a weak broad absorption band at 801.0 cm^{-1} which can be seen in all crystalline boron semiconducting samples, including boron and boron carbide and in all their samples of amorphous boron films, H_2 doped, C doped and C_2H_2 doped amorphous boron films, is associated with the short-range order common in all these forms of boron. Blum also states that the narrow absorption band at 2558.3 cm^{-1} is only formed in his H_2 and C_2H_2 doped films. Now Auger analysis has shown that my films contain no carbon. Therefore, it can be concluded that the broad weak band at 801 cm^{-1} is also due to the B:H bonds.

At around 2100 cm^{-1} there is a broad band in my samples as well as the bulk boron listed in Blum's table (see the table in Appendix 2). Blum cited the conclusion of J. Jaumann²⁵ saying that is due to an unknown impurity in bulk amorphous boron. They could not find what it was, even using SIMS, which is capable of detecting parts per million of impurities. Our Auger result could not give me any hint either. Therefore we conclude that either the conclusion cited by Blum is wrong or the amorphous CVD boron films deposited at high temperature is different from evaporated boron films deposited at room temperature. We conclude that the band is probably due instead to the a-B network itself or else is due to B:H bonds.

Interference fringes in the transmission spectrum of the thin film can overlap the absorption band, making the analysis difficult. The problem is accentuated with self-supporting films where there are substantial reflections from the back surface of the film. Thus using a thin boron self-supporting film, as a sample, is problematic. The example of the overlap is shown in Fig. 3.4. This effect is almost unobserved for a-B film on silicon substrate, which is used as a sample for the IR tests mentioned above, because there is little difference in the refractive index of silicon and boron.

3.3 Hydrogen Effusion Test

3.3.1 Introduction

Since CVD boron film is hydrogenated, when the sample is heated sufficiently the bond between boron and hydrogen will break allowing the hydrogen to escape where it can be measured^{26,27}.

Fig. 3.5 shows the hydrogen effusion test system. To make accurate measurements before beginning the test, the whole system should be evacuated and it should be verified that there are no leaks. After that the sample is heated to and maintained for a period at a given temperature to allow H₂ to form and diffuse from the sample. The holding temperature depends on the material used. In our case 800°C was required. Then the heater is removed, the system is cooled down to room temperature, the bottom tip of the container, which is shown in Fig. 3.5, is cooled with liquid nitrogen. Most gases which might conceivably

be emitted from the film, such as water vapor are condensed since they have higher boiling points than that of nitrogen. The exceptions are hydrogen, which is the object of the test, and a few inert gases which can be neglected compared with the hydrogen content. Thus the pressure measured is due entirely to the hydrogen emitted.

3.3.2 Calculation of Hydrogen Content

I use the ideal gas law to calculate the hydrogen content of the films. Since the pressure inside the tube remains much less than ambient pressure outside the tube this is a satisfactory approximation. When the pressure of hydrogen in the container has been measured, the following formula is used to get the mass of hydrogen emitted by the sample.

$$\frac{PV}{T} = nR = \frac{W}{2}R \quad (3.3.1)$$

where P indicates the pressure in the container, V, its volume, T, the temperature in Kelvin scale, R, the molar gas constant, W, the mass of the hydrogen emitted by the sample. With no other impurities the composition of a-B:H is B_xH_{1-x} . Thus,

$$\frac{1-x}{10.81x + (1-x)} = \frac{W}{m-M} \quad (3.3.2)$$

where M is the mass of silicon before deposition, m that after deposition, 10.81 the atomic weight of boron.

Solving the equations we can determine x.

3.3.3 Measurement Procedures Followed:

1. Test and adjust the system so that it will not leak;
2. Perform a blank run, that is, do a hydrogen effusion test for a bare silicon wafer using the steps below to determine the lowest limit for hydrogen composition;
3. Weigh the mass of the sample before and after boron coating is deposited;
4. Put the coated sample inside the container and evacuate the container until the pressure goes to the lowest value, approximately 10^{-3} torr for our double stage rotary pump;
5. Heat the container to 800°C ;
6. Cool the tip of the container with liquid nitrogen and get the reading of the inside pressure from the barometer;
7. Evacuate the container. Then heat it to the temperature of 50°C higher than the former high temperature;
8. Cool the tip of the container with liquid nitrogen and record the reading of the inside pressure from the barometer;
9. Repeat step 7 and 8 until there is no reading of pressure when container is cooled down. From the readings of pressure the mass of the hydrogen emitted can be found.

3.3.4 Result

Since there was no pressure rise in blank run (see Step 2 above), the pressure

reading is due only to the hydrogen emitted from the boron films. By solving equation (3.3.2) one can determine the content of hydrogen of the sample.

The following table indicates the results for the samples deposited at 1.25 volts of the mass flow controller which corresponds to a nominal flow of 50 sccm and the temperature distribution inside the reaction chamber discussed in Chapter II for a nominal temperature of 450°C.

location(inch)	composition	temp. in deposition(°C)
1	$B_{0.92}H_{0.08}$	352
2	$B_{0.56}H_{0.43}$	398
3	$B_{0.45}H_{0.55}$	424
4	$B_{0.33}H_{0.67}$	438
5	$B_{0.29}H_{0.71}$	449

Since the deposition rate beyond 5 inches decreases quickly I determined not to test the hydrogen content of the films from further in the reaction chamber.

Note that the samples towards the front of the reactor which are deposited at a lower substrate temperature actually have less hydrogen than those towards the back. It could be argued that hotter substrates should have less hydrogen since heat is required to break up B_2H_6 in the front of the reactor where deposition take place and heat "bakes out" hydrogen in the effusion test. Indeed the hydrogen content of amorphous silicon films decreases monotonically with increasing substrate temperature in cold wall reactors¹⁴.

Unfortunately when I did this experiment I could not measure the exact thickness of boron film samples. At first I did not find a good etchant for boron film and could not make steps in boron films. After I could make steps in boron films the stylus instrument in Electrical Engineering Department was in bad condition and the Wyko instrument could not tell the correct order of the interference fringes caused by the steps. I could not determined the thickness of boron films until I completed the hydrogen effusion experiments.

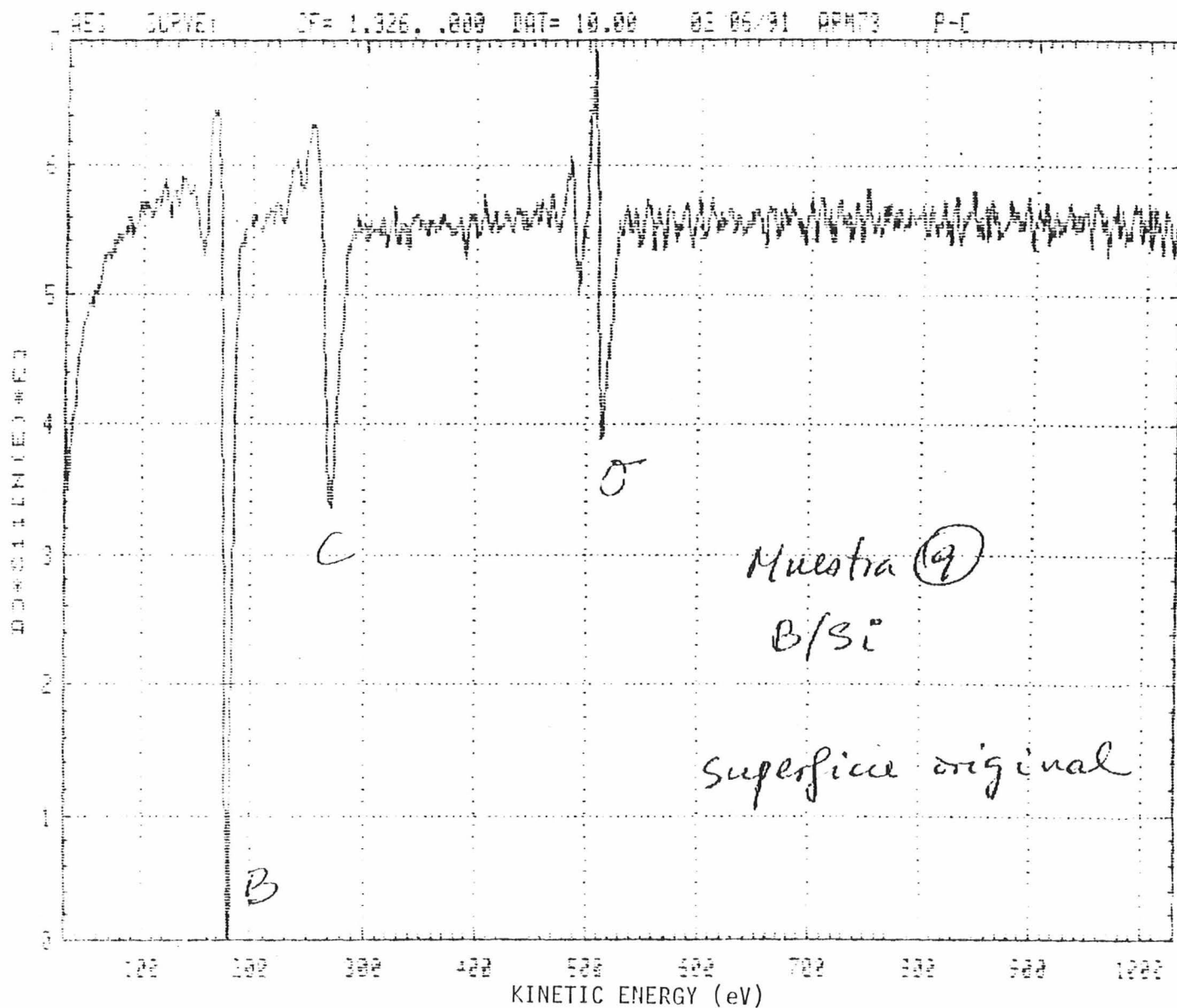


Fig. 3.1(a) The Auger spectrum indicates that the sample consists of boron, carbon and oxygen.

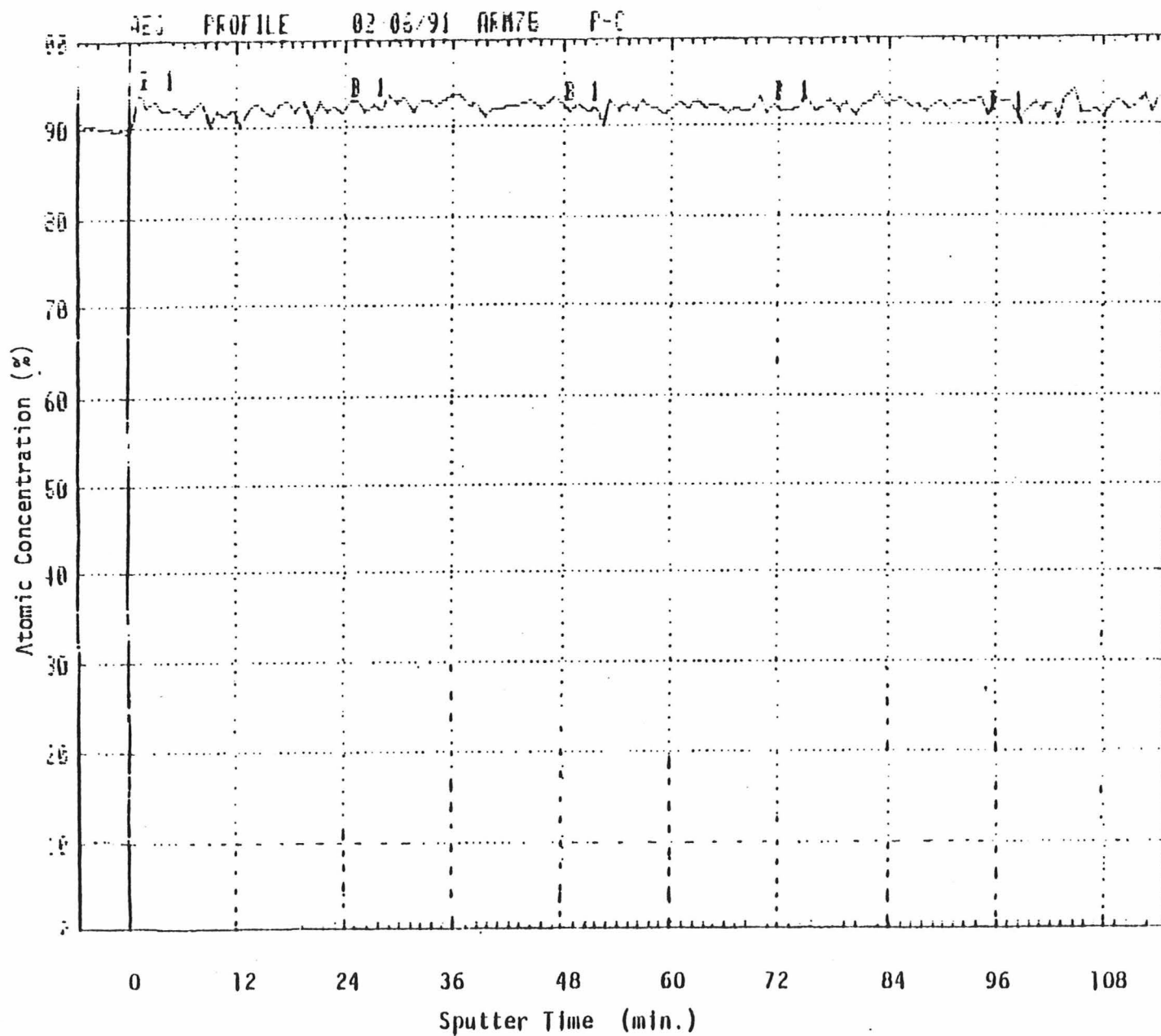


Fig. 3.1 (b) The Auger experimental plot of atomic concentration vs. sputtering time indicates that the sample consists of boron.

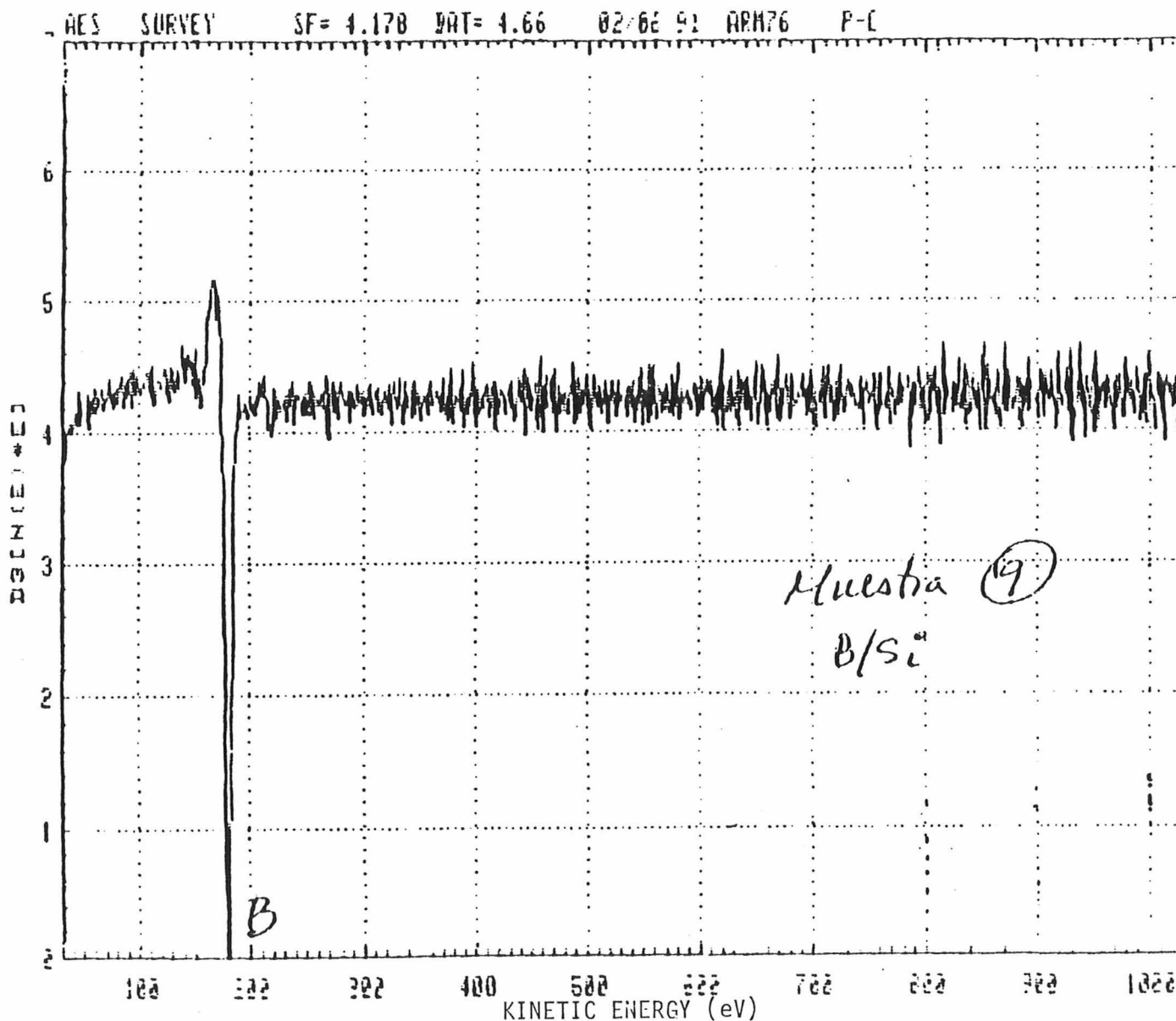


Fig. 3.1 (c) The Auger spectrum indicates that the sample only consists of boron after 120 minutes of sputtering.

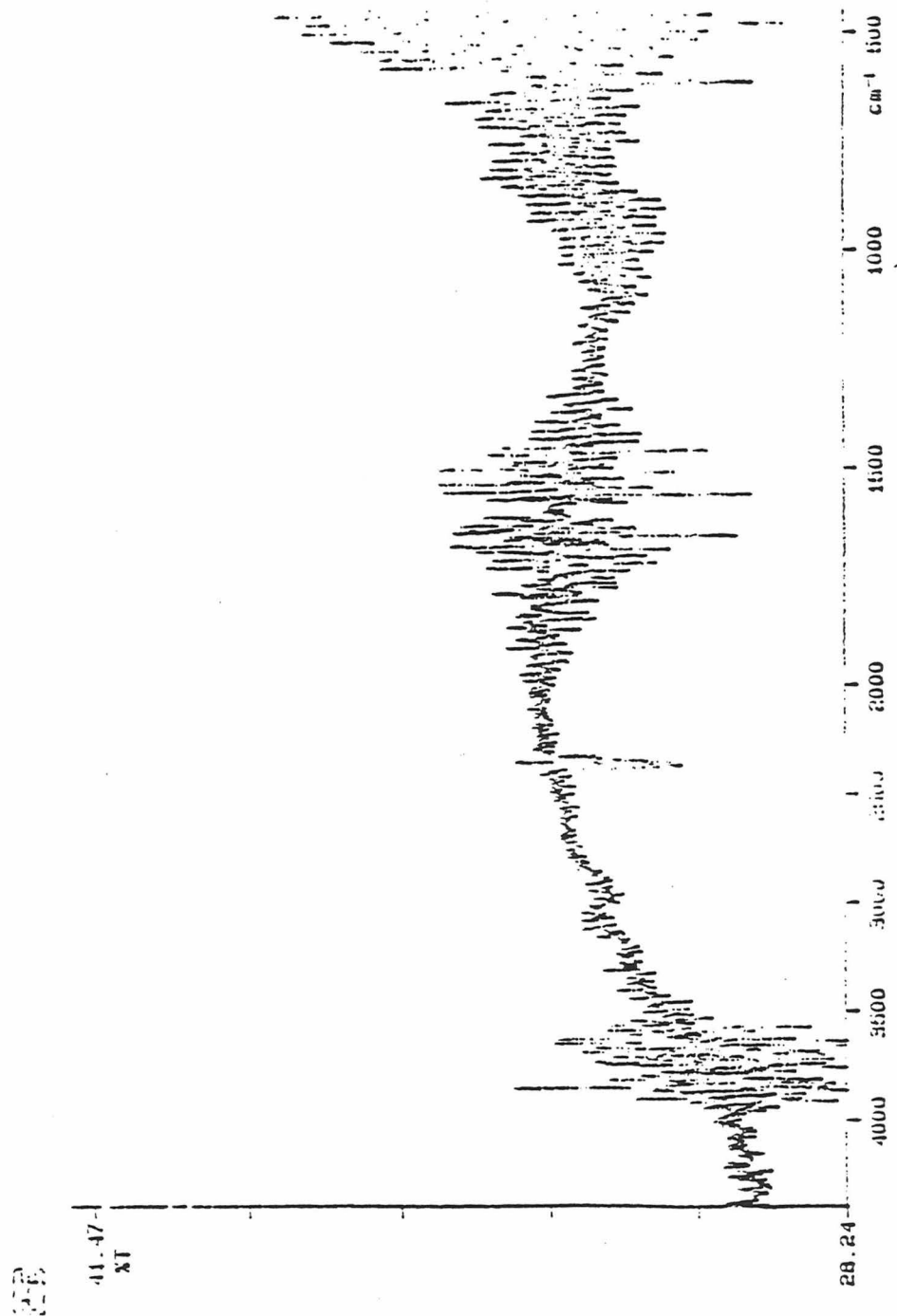
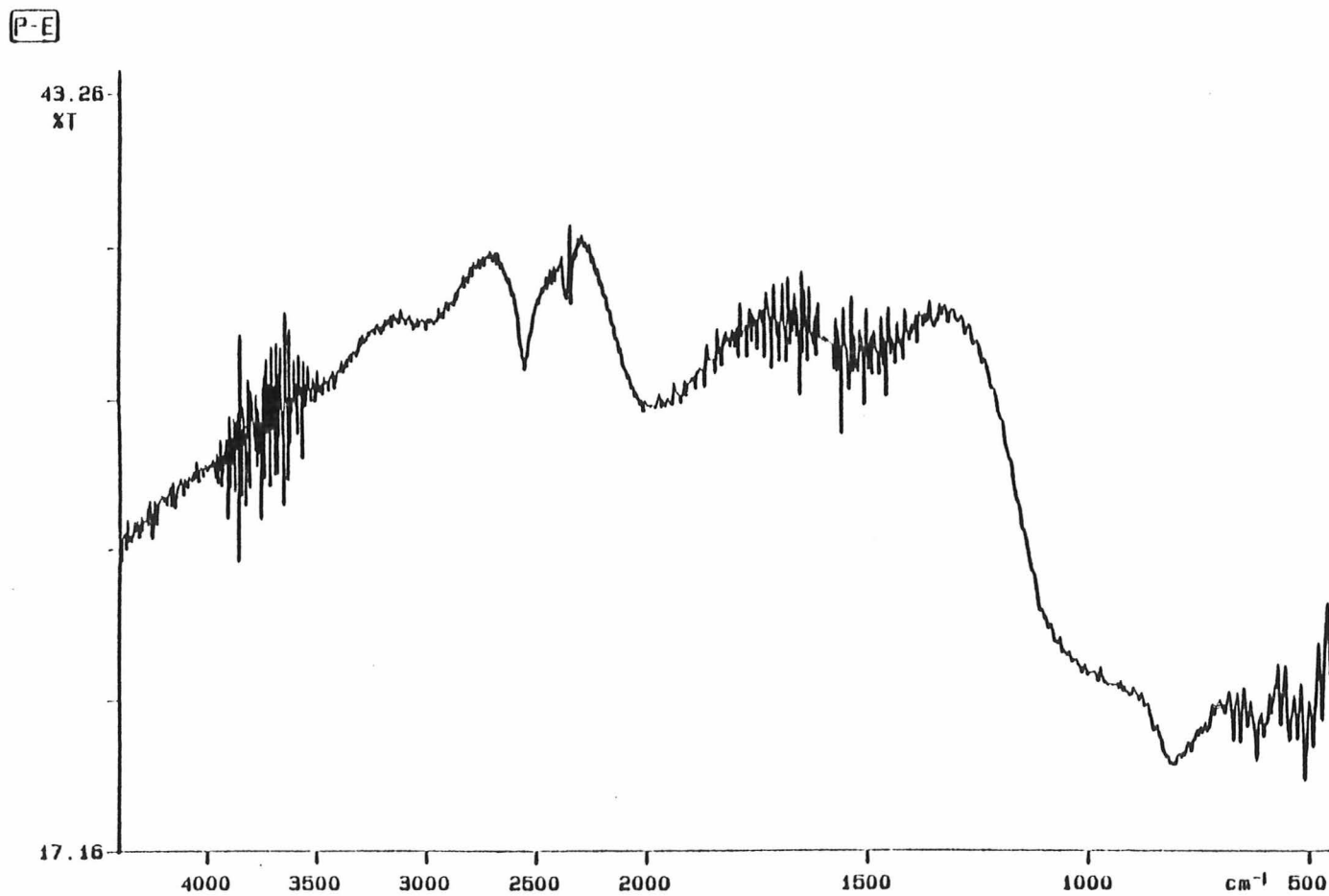
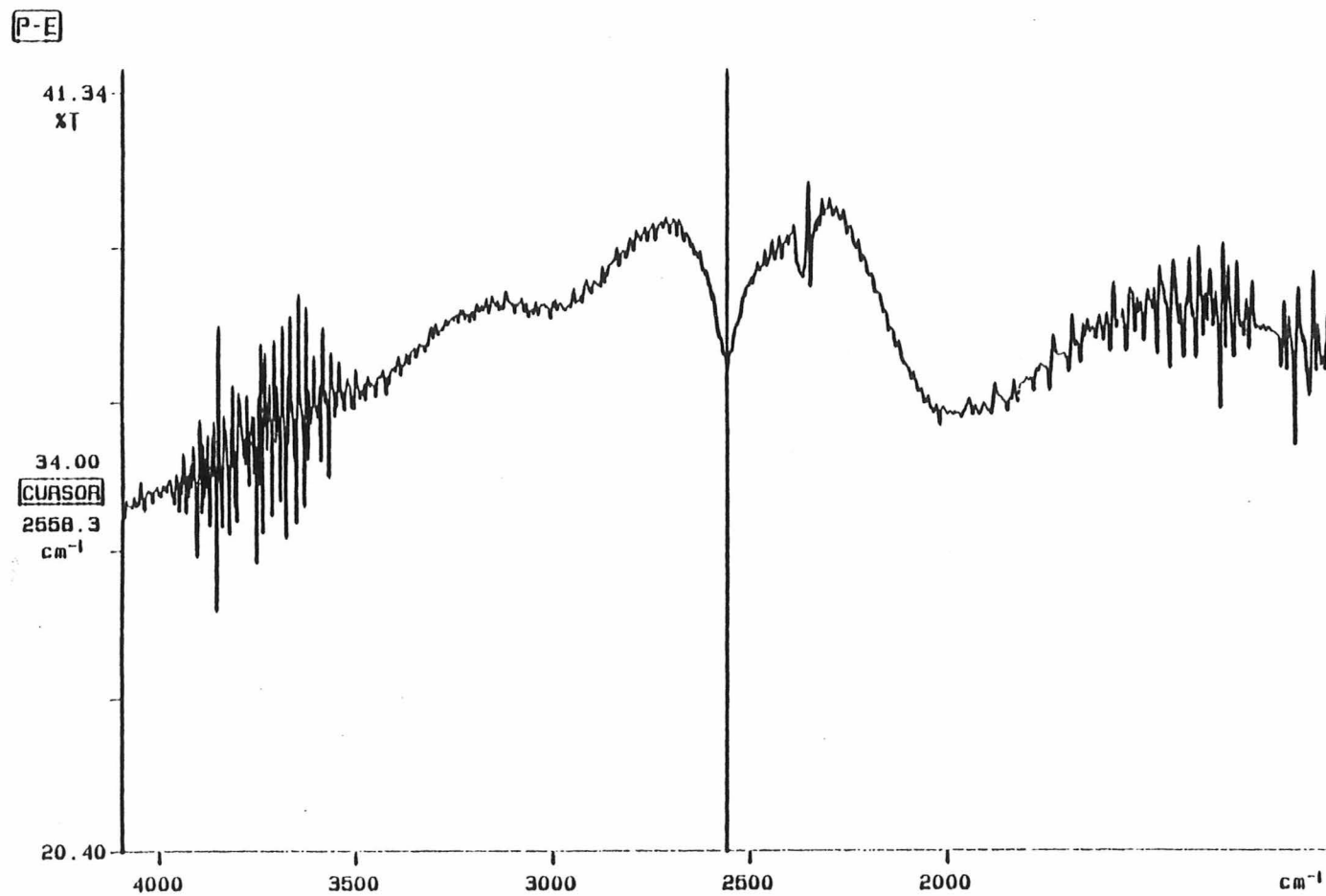


Fig. 3.2 IR Transmission spectrum of a silicon thin wafer with both sides polished.



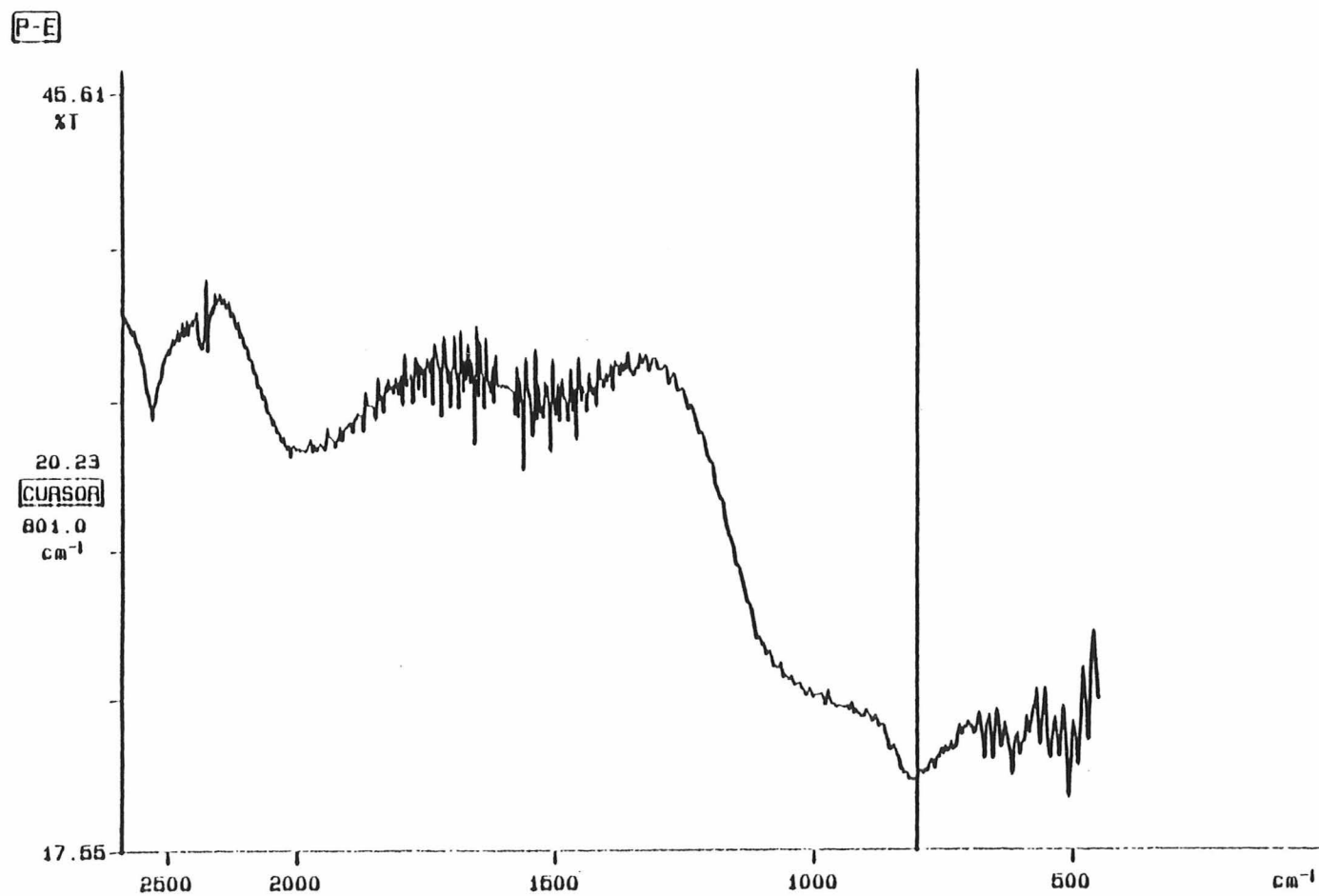
90/10/05 14:38
X: 1 scan, 4.0 cm^{-1}

Fig. 3.3(a) IR transmission spectrum of amorphous boron thin film on one side of a silicon thin wafer at room temperature;



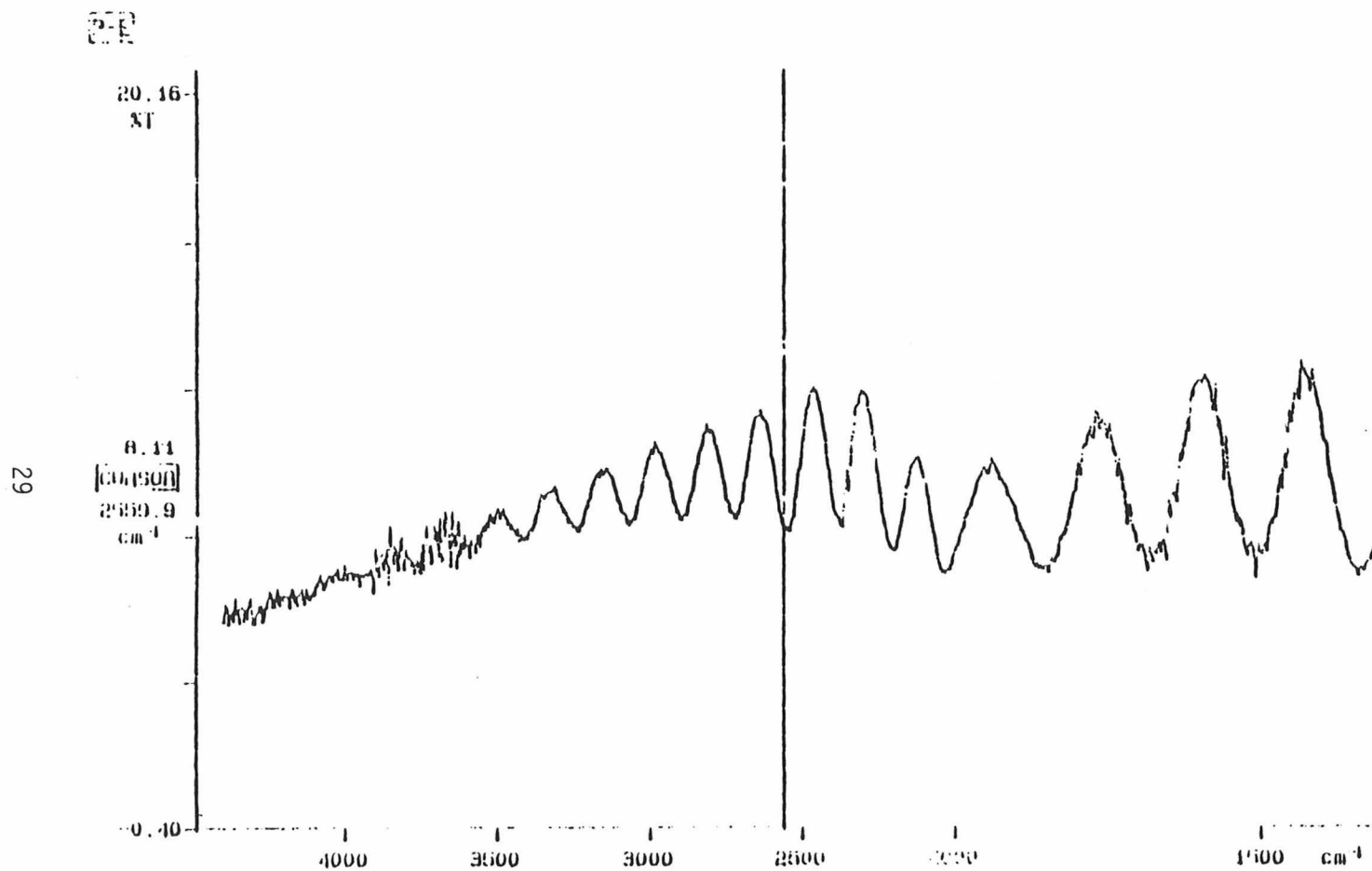
90/10/05 14:38
X: 1 scan, 4.0cm⁻¹

Fig. 3.3 (b) The cursor indicates a center of the absorption bands at 2558.3cm⁻¹;



90/10/05 14:38
X: 1 scan, 4.0cm⁻¹

Fig. 3.3(c) The cursor indicates a center of the absorption bands at 801.0cm⁻¹.



90/10/02 13:26
S: 1 scan, 4.0cm⁻¹

Fig. 3.4 IR transmission spectrum of an amorphous boron thin film. The interference fringes overlap the absorption bands.

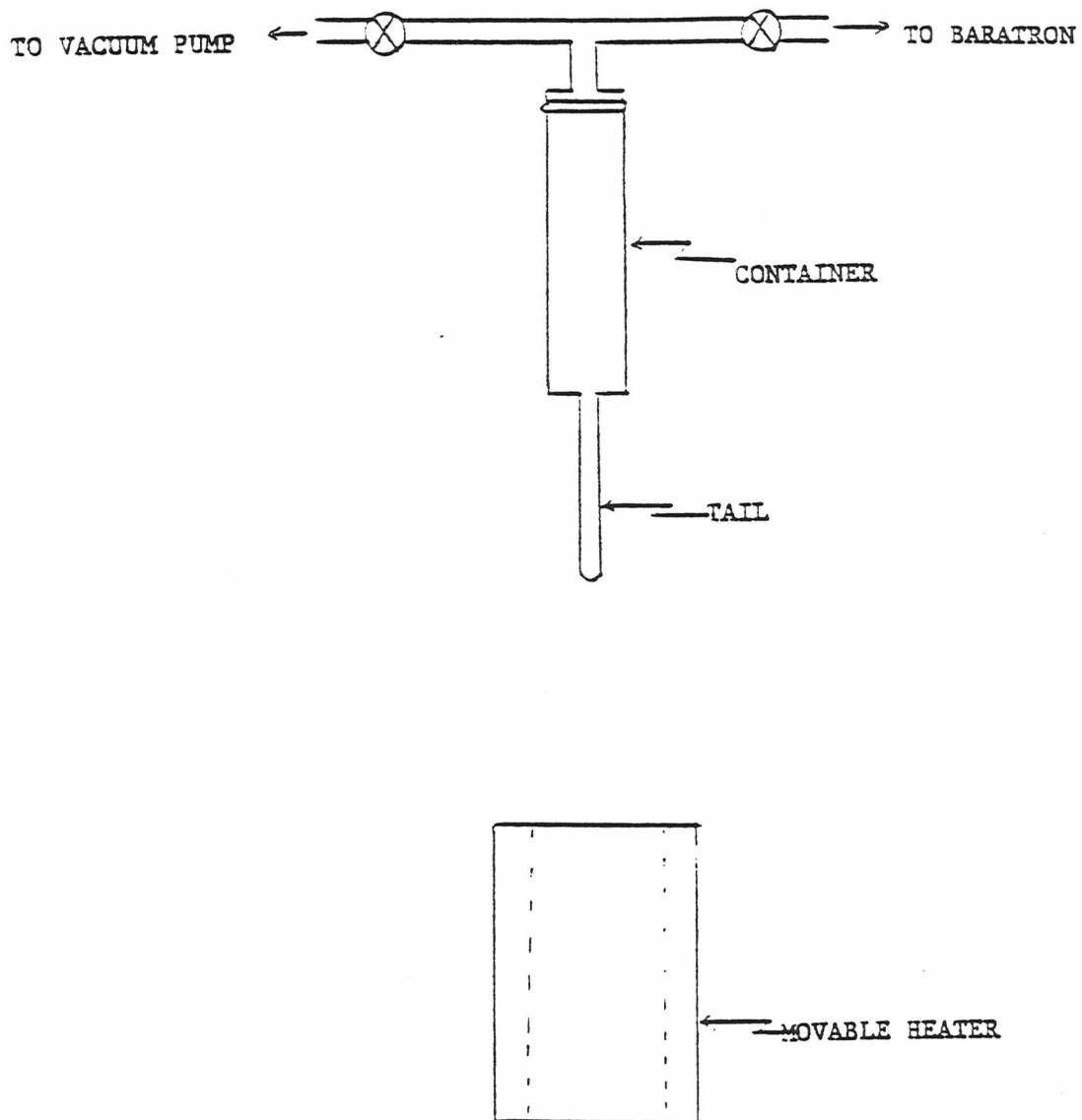


Fig. 3.5

System of hydrogen effusion test

IV. MEASUREMENT OF REFRACTIVE INDEX FOR AMORPHOUS BORON THIN FILM

4.1 Introduction

An optical method is used here to determine the refractive index n and k defined in the visible and near infrared regions. This method works for materials such as amorphous silicon and boron thin films deposited on transparent substrates, in this case pyrex microscope slides. The thickness of the film can also be determined at the same time provided the films are uniform, smooth and adhere well to the substrate.

The method suggested by Swanepoel²⁸ to determine thickness and optical constant is good for transparent regions and weak or medium absorption regions where interference fringes exist. Swanepoel took an amorphous silicon film or a hydrogenated a-Si:H film as an example where interference fringes cover the whole near infrared and visible. However, for boron films the interference fringes gradually disappeared in the visible region. This means that the extinction coefficient k becomes larger in this region. Also as shall be shown a-B:H has a shallow absorption edge. Thus a new method was developed to use both transmittance and reflectance of the sample to find n and k .

A reflectance formula related to n and k at any incident angle was derived. The Perkin Elmer 320 spectrophotometer can give the reflectance and transmittance of the sample at visible and near infrared light. It is easy to use

computer iteration techniques to determine its n and k from the reflectance and transmittance of the sample.

4.2 Theory

Considering the thick microscope slide alone in the absence of a film, the interference-free transmission is given by the well known expression²⁸:

$$T_s = \frac{(1 - R)^2}{1 - R^2},$$

where

$$R = \left[\frac{s - 1}{s + 1} \right]^2,$$

s is the optical index of the microscope slide. Then

$$s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1 \right)^{\frac{1}{2}} \quad (4.1)$$

The practical situation for a thin film on a transparent substrate is shown in Fig. 4.1. The film has thickness d and complex refractive index $\hat{n} = n - ik$, where n is the refractive index and k the extinction coefficient. There are four regions in the transmittance spectrum: transparent region, weak absorption region, medium absorption region, and strong absorption region (see Fig. 4.2) for the system of an absorbing thin film on a thick, but finite, transparent substrate²⁸. In the transparent region, such as infrared light region for amorphous boron and silicon, the analysis used follows Swanepoel. When k is close to zero, the transmittance is given by the equation²⁸:

$$T = \frac{Ax}{B - Cx \cos \phi + Dx^2} \quad (4.2)$$

where

$$A = 16n^2s \quad (4.3a)$$

$$B = (n+1)^3(n+s^2) \quad (4.3b)$$

$$C = 2(n^2-1)(n^2-s^2) \quad (4.3c)$$

$$D = (n-1)^3(n-s^2) \quad (4.3d)$$

$$\phi = 4\pi nd/\lambda \quad (4.3e)$$

$$x = \exp(-\alpha d) \quad (4.3f)$$

$$\alpha = 4\pi k/\lambda \quad (4.3g)$$

The extremes of the interference fringes can be written as

$$T_{max} = \frac{Ax}{B - Cx + Dx^2} \quad (4.4)$$

$$T_{min} = \frac{Ax}{B + Cx + Dx^2} \quad (4.5)$$

In the transparent region $\alpha = 0$ or $x = 1$. Substituting equation (4.3) in equation (4.5) for $x=1$ yields

$$T_{min} = \frac{4n^2s}{n^4 + n^2(s^2 + 1) + s^2}$$

or

$$n = [M + (M^2 - s^2)^{\frac{1}{2}}]^{\frac{1}{2}} \quad (4.6)$$

where

$$M = \frac{2s}{T_{min}} - \frac{s^2 + 1}{2} \quad (4.7)$$

In the region of weak and medium absorption $\alpha \neq 0$ and $x < 1$. Subtracting the reciprocal of equation (4.4) from the reciprocal of equation (4.5) yields the following expression that is independent of x .

$$\frac{1}{T_{min}} - \frac{1}{T_{max}} = \frac{2C}{A} \quad (4.8)$$

substituting equation (4.3) into (4.8) and solving for n yields

$$n = [N + (N^2 - S^2)^{1/2}]^{1/2},$$

where

$$N = 2x \frac{T_{max} - T_{min}}{T_{max} T_{min}} + \frac{s^2 + 1}{2} \quad (4.9)$$

The basic equation for interference fringes is

$$2nd = m\lambda, \quad (4.10)$$

where m is an integer for minima and half integer for maxima since the index of the film is larger than that of microscope slides.

The index of refraction at two successive extrema is related by the equation

$$\frac{n_2}{\lambda_2} = \frac{n_1}{\lambda_1} + \frac{1}{4d} \quad (4.11)$$

Using the above equation we can get the thickness of the film.

According to Swanepoel if we consider the slit width correction we will be able to get the thickness and n to within 1% error in the transparent region, with a little bit larger error in the weak and the medium absorption regions.

In the region of strong absorption $x \ll 1$ equation (4.2) becomes

$$T_0 \simeq Ax/B$$

or

$$x = \frac{(n+1)^3(n+s^2)}{16n^2s} T_0 = \exp(-\alpha d) \quad (4.12)$$

Note that the interference fringes disappear in this region and there is no way to calculate n and x independently. Here we derived the reflectance formula at any incident angle so that we can try to use another way to find n and k in this region.

From branch 1 in Fig. 4.3 the complex number $\hat{r}_1$ of the Fresnel coefficient for reflection²⁹

$$\begin{aligned} \hat{r}_1 &= \hat{r}_{12} + \hat{t}_{12}\hat{r}_{23}\hat{t}_{21}e^{i\beta} + \hat{t}_{12}\hat{r}_{23}\hat{r}_{21}\hat{r}_{23}\hat{t}_{21}e^{2i\beta} + \dots \\ &= \frac{\hat{r}_{12} + \hat{r}_{23}(\hat{t}_{12}\hat{t}_{21} - \hat{r}_{12}\hat{r}_{21})e^{i\beta}}{1 - \hat{r}_{21}\hat{r}_{23}e^{i\beta}} \end{aligned}$$

where $\hat{r}_{12}$ and $\hat{t}_{12}$ are called the Fresnel coefficients between the first layer and second layer, $\hat{r}_{23}$ and $\hat{t}_{23}$ the Fresnel coefficients between the second layer and third layer ... etc. The complex number of β is the phase difference. Since²⁹

$$\hat{r}_{12} = -\hat{r}_{21}$$

$$\hat{r}_{12}^2 + \hat{t}_{12}\hat{t}_{21} = 1$$

Thus,

$$\hat{r}_1 = \frac{\hat{r}_{12} + \hat{r}_{23}e^{i\beta}}{1 + \hat{r}_{12}\hat{r}_{23}e^{i\beta}}$$

The Fresnel coefficients for the s-polarized light are as follows:

$$r_{12s} = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2}$$

$$r_{23s} = \frac{n_2 \cos \theta_2 - n_3 \cos \theta_3}{n_2 \cos \theta_2 + n_3 \cos \theta_3}$$

The phase difference between them becomes

$$\beta = 2d \frac{\omega}{c} (p + iq),$$

where

$$p = \sqrt{\frac{1}{2}[(K_r - K_1 \sin^2 \theta_1) + \sqrt{(K_r - K_1 \sin^2 \theta_1)^2 + K_i^2}]}$$

$$q = \sqrt{\frac{1}{2}[-(K_r - K_1 \sin^2 \theta_1) + \sqrt{(K_r - K_1 \sin^2 \theta_1)^2 + K_i^2}]}$$

Using Snell's law $\hat{n} \sin \hat{\theta} = n_1 \sin \theta_1$, we can find

$$K_r = n_2^2 - k_2^2;$$

$$K_1 = n_1^2;$$

$$K_i = 2n_2 k_2,$$

where n_2 and k_2 are the real and imaginary part of the refractive indexes of the absorbing thin film layer. Thus, the reflectance of branch 1 becomes

$$R_{1s} = r_{1s} r_{1s}^*.$$

In a similar way for branch 2 we get

$$\hat{r}_{2s} = \frac{(1 - \hat{r}_{12s}^2)(1 - \hat{r}_{23s}^2)\hat{r}_{31s}e^{i(A+\beta)}}{1 - \hat{r}_{21s}\hat{r}_{23s}e^{i\beta}}$$

the phase difference of the microscope slide becomes

$$A = \frac{4\pi d}{\lambda} \sqrt{s^2 - \sin^2 \theta_1}$$

Branch 1 is the main part of the reflection. Branch 2 is only a small part of the reflection, being 1 to 4 percent of the reflectance for amorphous boron film on 7059 glass plate. The other branches of reflection are so small that all of them can be neglected.

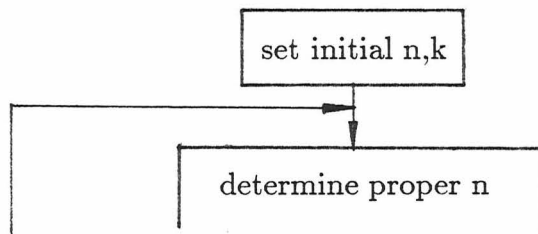
$$\hat{r}_s = \hat{r}_{1s} + \hat{r}_{2s}$$

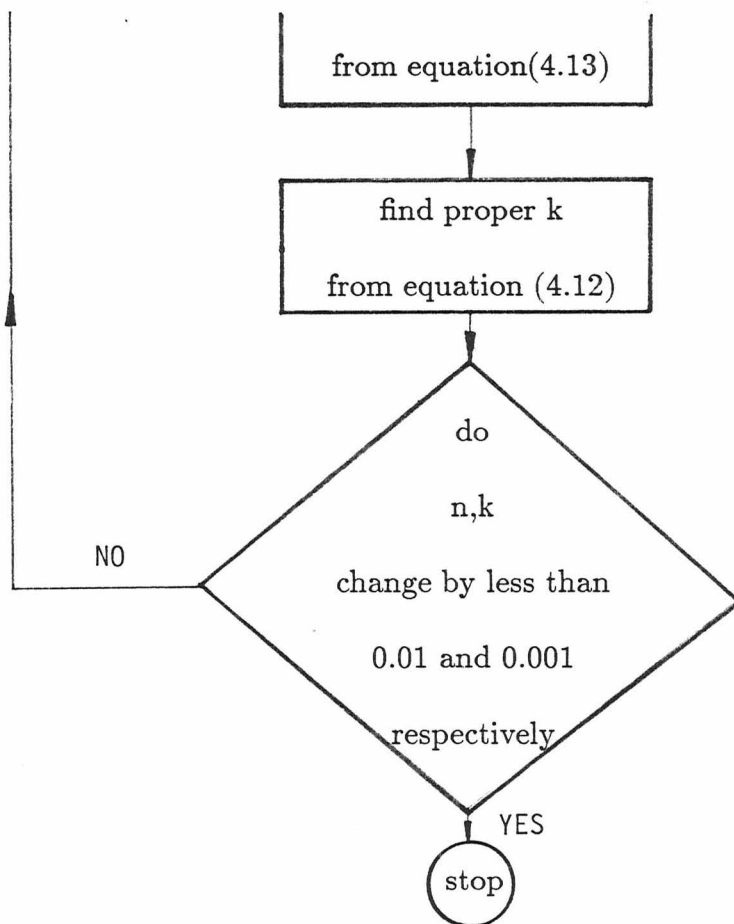
$$R_s = \hat{r}_s \hat{r}_s^* \quad (4.13)$$

In front of the detector we put a polarizer so that only the light with s polarity can pass through. Thus we make the calculation easier. To apply the above formula to find the reflectance we can build a simple device which can sit in Perkin Elmer 320 spectrophotometer. The optical structure is shown at Fig. 4.4. The two mirrors are set up properly so that the whole system becomes symmetric and the incident angle can easily be found.

4.3 Data Processing

For the transparent region we used the Swanepoel's method to find the refractive index n and the thickness d . For the regions where k cannot be neglected a basic schematic of the procedure is as follows:





The program is listed in Appendix 3. Some steps are discussed in detail as follows:

Step (1): Try to find the index of refraction of the film. For the transparent region we can use Eq (4.6), (4.7) and (4.10) to find the n and the thickness d . For the absorption region, we still use Eq. (4.8), (4.10) to find the initial n , set initial $k = 0.001$ and use the thickness d we have already obtained, then go to the second step.

It is important to choose initial n and k properly. If the initial n and k are close to the true values, the iteration will converge quickly, otherwise problems might happen.

Step (2): We use Eq. (4.13) and iteration techniques to find the proper n .

If the initial n and k are properly chosen there exists a rapid convergence of n and k in the strongly absorbing region. The curve at Fig. 4.5 is the solution of Eq. (4.13) for $R = 0.293$. The curve b is the solution for Eq. (4.12) for $T = 0.213$. They are almost perpendicular to each other and thus very easy to converge to one point.

4.4 Test and Discussion

The best way to check a method is to see how close the true values and measured values are. Fig. 4.6 and Fig. 4.7 are the transmission and reflection curves of amorphous silicon. We found that at the following wavelengths there exist fringes in the reflectance plot but not in the transmittance plot. Thus, using the method mentioned above we can get the following data:

$\lambda(nm)$	n_t	k_t	n_m	k_m
605	4.26	0.0946	4.22	0.0952
577	4.35	0.1517	4.35	0.1500
557	4.42	0.228	4.43	0.229

From the above table, the relative error is less than 1%. As long as we can still tell the transmittance of the sample we can get n and k for shorter wavelengths.

It should be noted that since the reflectance consists of many branches, the values of both sides of Eq. (4.13) are close but not exactly equal.

Since Swanepoel discussed the transmission in great detail, here we only focus our attention on the reflection. There are some factors which will influence the data measured. The slit width of the instrument is one of the factors. Fig. 4.8(a) is the reflectance curve with a slit width of $1\text{ nm} \pm 1\text{ nm}$. (Note that on this and the following figures the dotted lines indicate the curves measured; solid curves indicate the theoretical curves.) Fig. 4.8(b) is the reflectance curve with a slit width of $1\text{ nm} \pm 4\text{ nm}$. We can see that when the slit width becomes larger, the intensities of valleys will change, but the locations of these extrema do not change at all.

The uniformity of the film will also influence the data measured. Fig. 4.9 is the reflectance curve for the boron thin film with a thickness of $500\text{ nm} \pm 10\text{ nm}$. We can see that the nonuniformity of thickness will also influence the intensity of the extrema. From that we know that it is better to choose the data at the points where the extrema of the reflectance would not happen.

Surface roughness is another factor which will influence the data measured. A rough surface will scatter the light so as to weaken the reflectance. The samples we tested have a root mean square roughness of 1.75 nm (see Fig. 4.10). I think that the error caused by the surface roughness must be negligible.

The calibration of the mirror reflectance is also important to the data measured.

This is a good method for finding n and k . It expands the range of measure-

ment compared to the method suggested by Swanepoel. It is easier to design and build the mirror device and get more accurate measurement compared to the method suggested by Kenneth A. Epstein³⁰. This method is especially good for some materials such as amorphous CVD boron thin films which have some reflectance fringes in the visible region and some transmittance fringes only in the near infrared region.

4.5 Experimental Results

The following table (on page 42) indicates n and k for the thin film deposited when the wafer located 2 inches away from the entrance of the hot zone and the mass flow controller is at 1.25 volts. The furnace was set at 450°C. Thus, the following expression can be found:

$$n = \frac{471.02}{\lambda^{1.01}} + 2.34$$

Similarly the refractive index of n and k for the thin films deposited at 3 inches and 4 inches from the entrance of the hot zone are given in Appendix 4.

From the above results of the hydrogen effusion test and the measurement of refractive index it is found that the boron films deposited with larger n and smaller k must contain more hydrogen. This conclusion is in agreement with the results published by Koun Shirai and Shun-ichi Gondapaper¹⁰ in May, 1990.

However, it is customarily thought that boron-hydrogen bonds are transparent to light, e.g. B_2H_6 is transparent. Thus if the sample of amorphous boron contains more hydrogen, n and k should both be smaller. This is what is

$\lambda(nm)$	n	k
1762	2.64	0.012
1412	2.64	0.022
1212	2.70	0.031
1040	2.72	0.044
854	2.81	0.065
797	2.87	0.089
709	3.01	0.124
637	3.17	0.167
550	3.19	0.243
520	3.20	0.275
490	3.25	0.314
470	3.30	0.344
450	3.34	0.378

seen in the a-Si:H and a-C:H system, for example.

It is very hard to explain this quantitatively why there is a contradiction between the result of measurement and the expectation. But the author of the paper¹⁰ mentioned above did not explain why. I can only try to figure it out qualitatively.

According to the electromagnetic theory there is a formula³¹ for a solid, whether or not it is crystal or amorphous, as follows:

$$\frac{n^2 - 1}{n^2 + 1} = \frac{Nq_e^2}{3\epsilon m_e} \sum_j \frac{f_i}{\omega_{0i}^2 - \omega^2 + ir_i\omega}, \quad (4.14)$$

where r is the damping coefficient, ω_{0i} the resonant frequency, f_i the number of oscillators having natural frequency ω_{0i} per unit volume, m_e the mass of electron, q_e the charge of electron, ϵ the permittivity of the material.

The variables f , ω_0 and r are quite different between boron and hydrogen, but N , the number of electrons in a unit volume, might have significant influence on the right side value of equation (4.14). Because a hydrogen atom is smaller in size than a boron atom and amorphous material can change its bond angles, the volume of the boron film would not change substantially when it is interstitially doped with much hydrogen. That causes N to be larger so that the value of the right side of equation (4.14) becomes larger and n would, evidently, be larger too since the left side of equation (4.14) can be written as follows:

$$\frac{n^2 - 1}{n^2 + 1} = 1 - \frac{2}{n^2 + 1}.$$

This viewpoint has not been verified by experiment since it is very difficult to find the exact volume of the thin film. Anyway this is worth studying in theory because it is very surprising that k would become lower, i.e., more transparent, and n larger, i.e., more reflective, when boron is doped with hydrogen. Note that it is the second example of how a-B:H is at variance with known hydrogenated amorphous semiconductors like a-Si:H and a-C:H.

4.6 Tauc Plots of Boron Films

The most notable characteristic of semiconductors is that they possess band gaps. This is true for amorphous as well as crystalline semiconductors. The Tauc plot is a way of defining a band gap for amorphous semiconductors.

The absorption of the visible light by the semiconductors is due to interband transitions. The absorption depends on the density of states in the valence and conduction bands. Tauc assumed that above the exponential tail electronic states at higher photon energies of have parabolic dependence on electron energy (see Fig. 4.10), i.e. $N(E) \sim E^{\frac{1}{2}}$. Tauc then derived³²:

$$(\alpha d \hbar \omega)^{\frac{1}{2}} = B^{\frac{1}{2}}(\hbar \omega - E_0),$$

where d is the thickness of the film, B is a constant, $E = \hbar \omega$, α is mentioned in the previous section. This means that plotting of $\sqrt{\alpha E}$ versus E should give a straight line. Its intercept on the x axis is E_0 , the optical band gap.

The same relation has been derived by Davis and Mott³³. Their assumptions, however, are somewhat different from those used in Tauc's model.

Tauc plots³² have been used to find the optical energy gap for a variety of chalcogenide films and amorphous tetrahedral materials like amorphous silicon^{34,35}. Using Tauc plots, however, to study CVD boron film has lagged.

Fig. 4.11 is the Tauc plots of the three samples mentioned above. From it the optical energy gap for each sample can be found respectively. The following table lists the results for a-B:H deposited at a nominal furnace temperature of 450°C.

location (inch)	hydrogen content	optical energy gap (eV)	thickness (nm)
2	$B_{0.56}H_{0.43}$	1.36	668
3	$B_{0.45}H_{0.55}$	1.18	866
4	$B_{0.33}H_{0.67}$	1.09	559

This table shows that the hydrogen content will affect the optical energy gap of the amorphous boron films. The larger the hydrogen content the smaller their optical energy gap which is, as was mentioned, at variance with more commonly studied amorphous semiconductors.

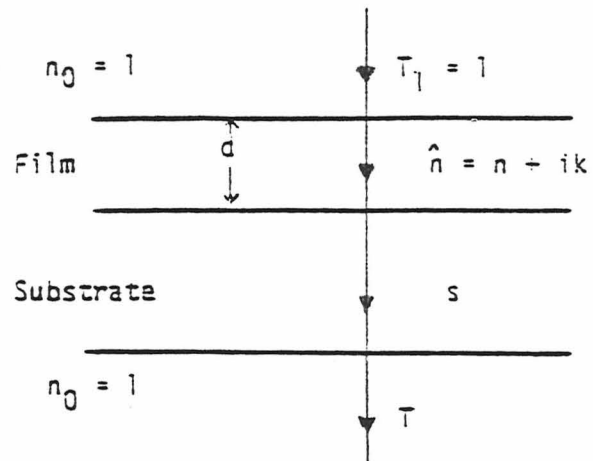


Fig. 4.1 The optical diagram for a thin film on a transparent substrate.

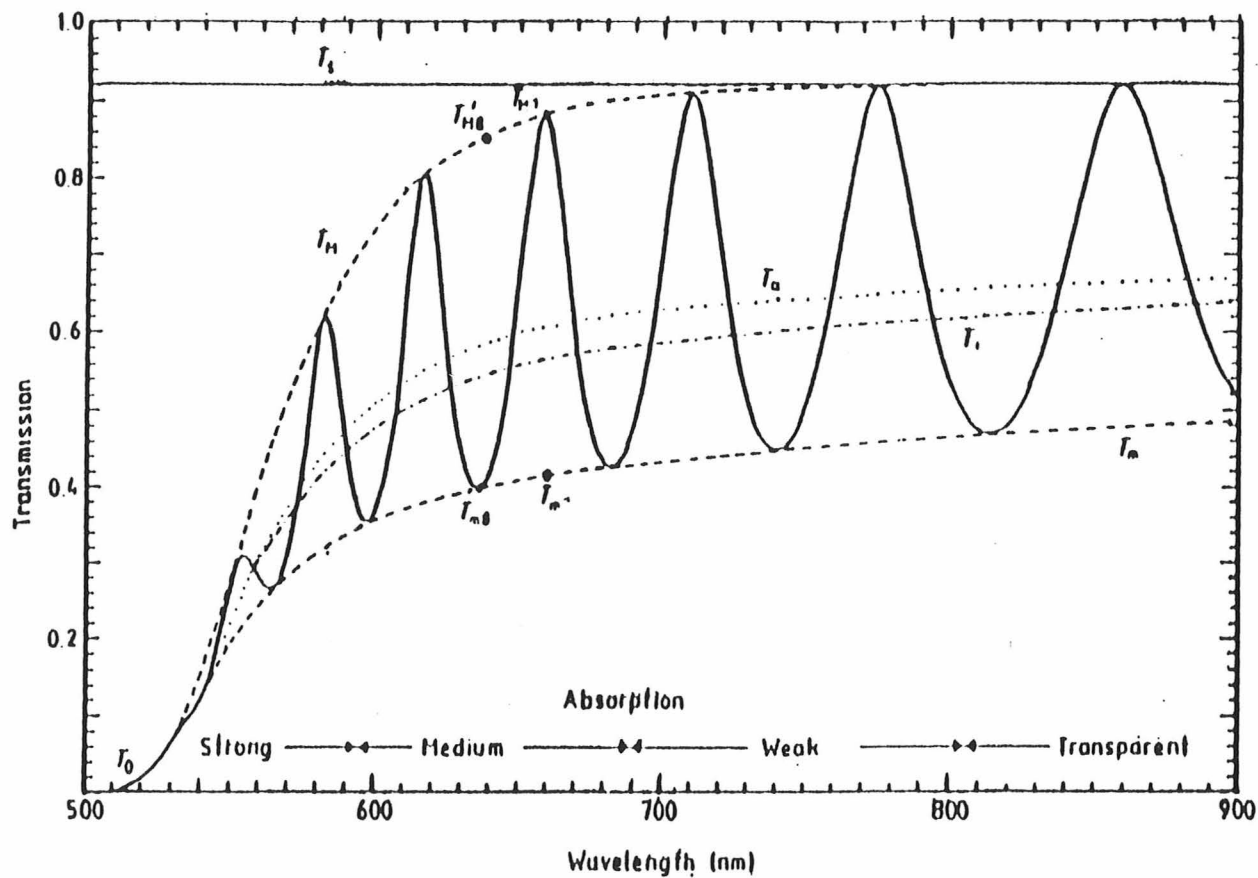


Fig. 4.2 Simulated transmission spectrum (full curve) for a $1\ \mu\text{m}$ film of $\alpha\text{-Si:H}$ on a finite glass substrate with transmission T_0 . Curves T_M , T_a , T_i and T_m according to the text.

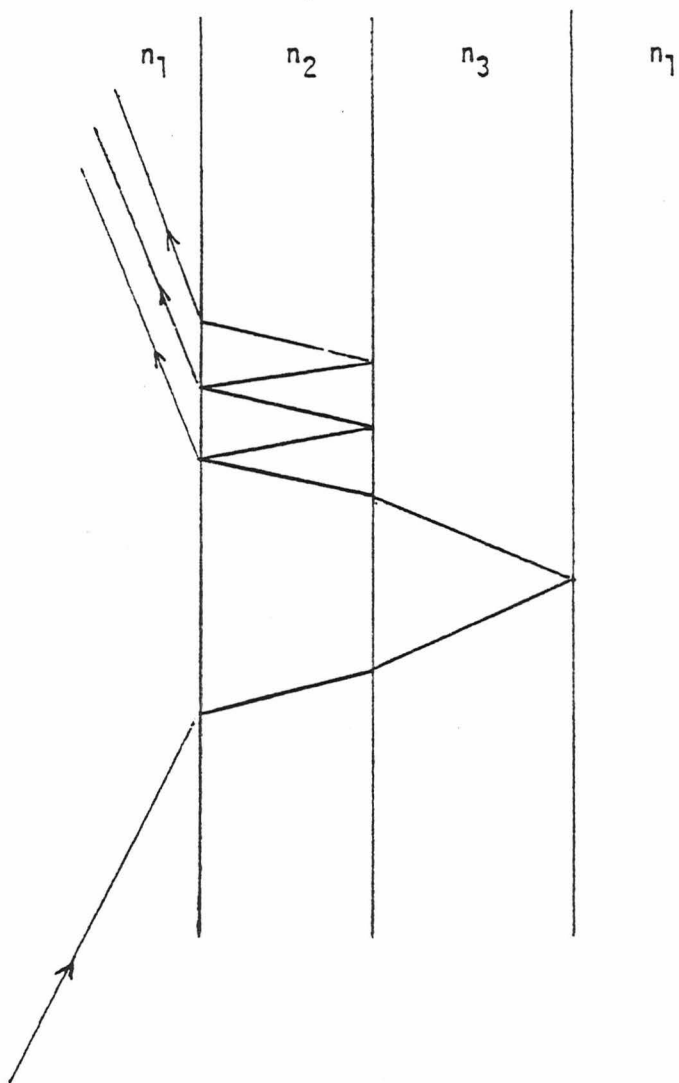


Fig. 4.3(b) Branch 2 of the multiple reflections of an incident ray.

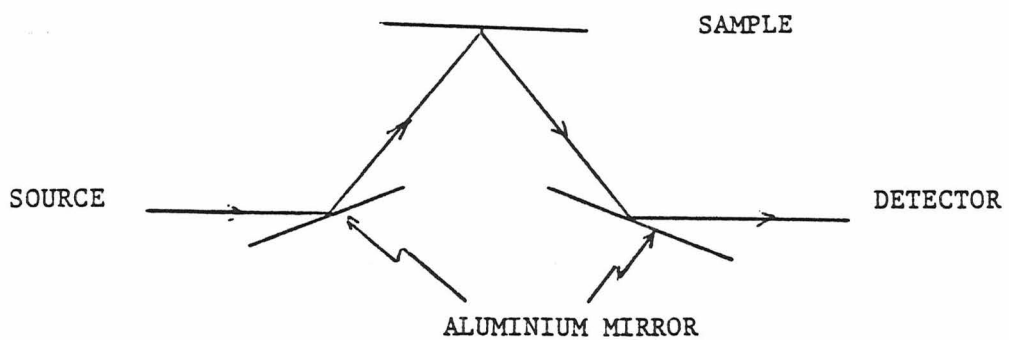


Fig. 4.4 The reflection system for the measurement

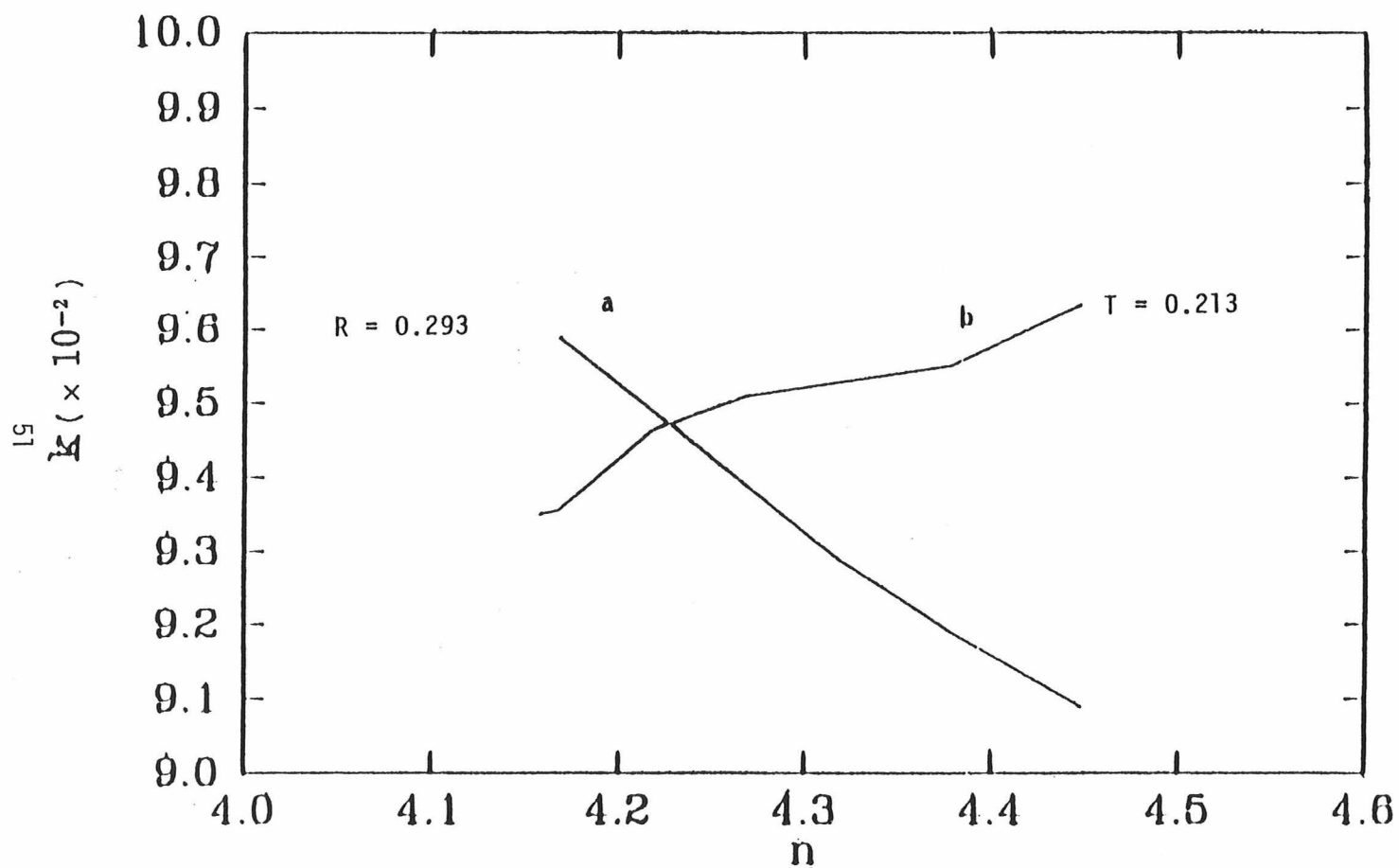


Fig. 4.5 Graphic solution of Eq.4.12(curve b) and Eq.4.13(curve a) for $R = 0.293$ and $T = 0.213$.

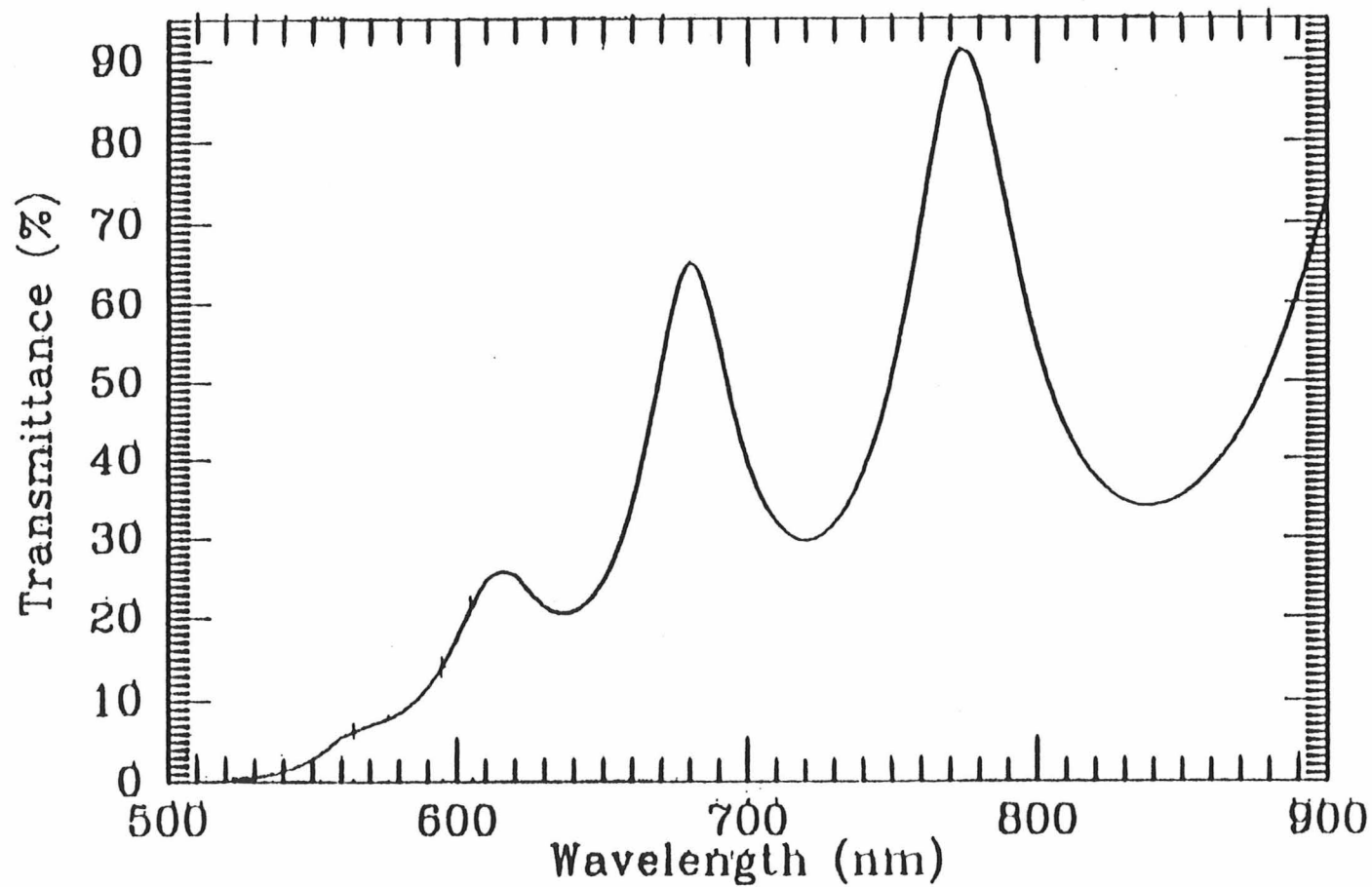


Fig. 4.6 Simulated transmission curve for the amorphous silicon film of 500nm thickness.

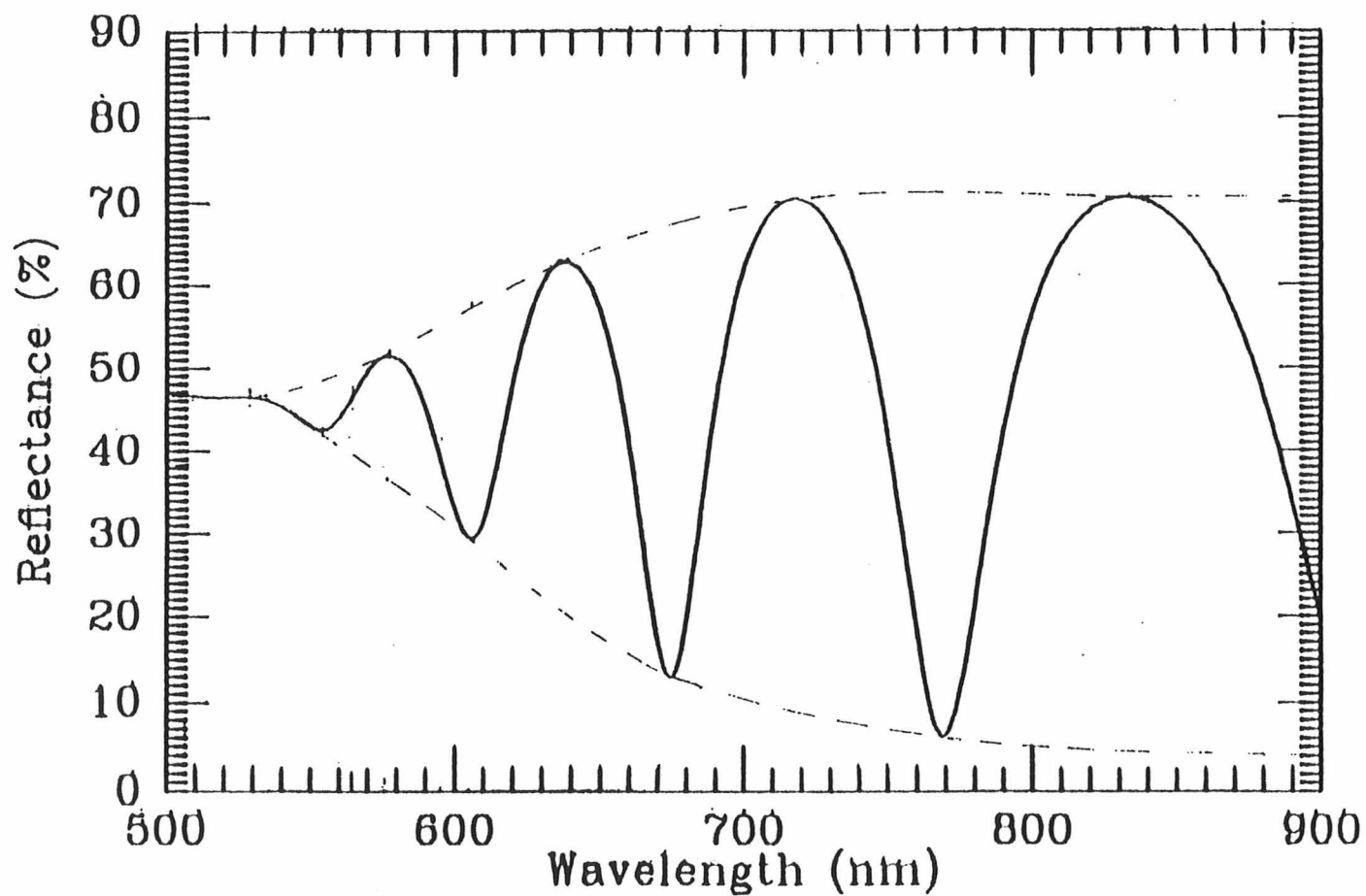


Fig. 4.7 Simulated reflectance curve for the amorphous silicon film of 500nm thickness.

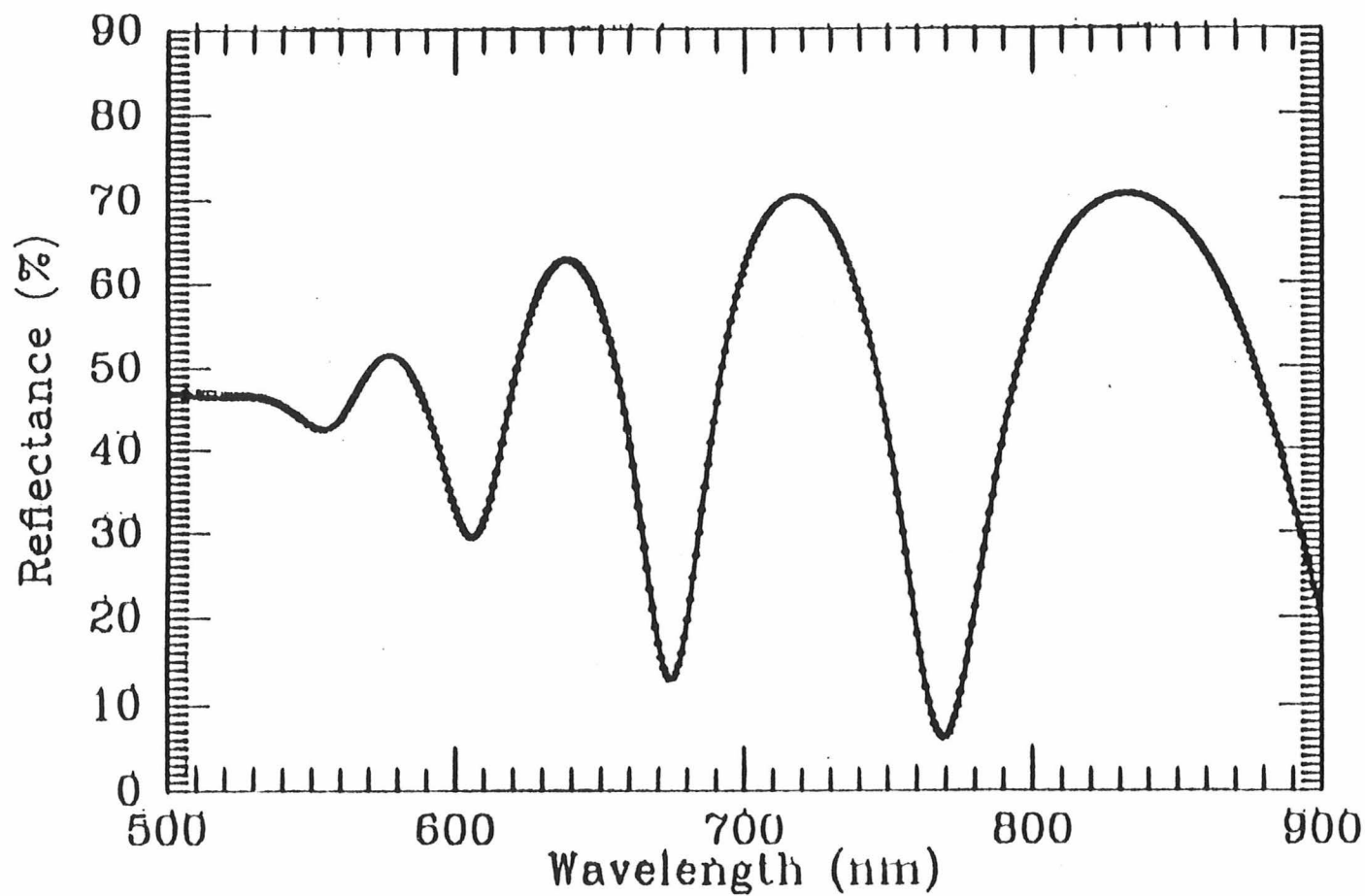


Fig. 4.8 (a) Simulated reflectance for a slit width of 1nm (dotted curve) compared to that of zero slit width (full curve) for a silicon film of 500nm thickness.

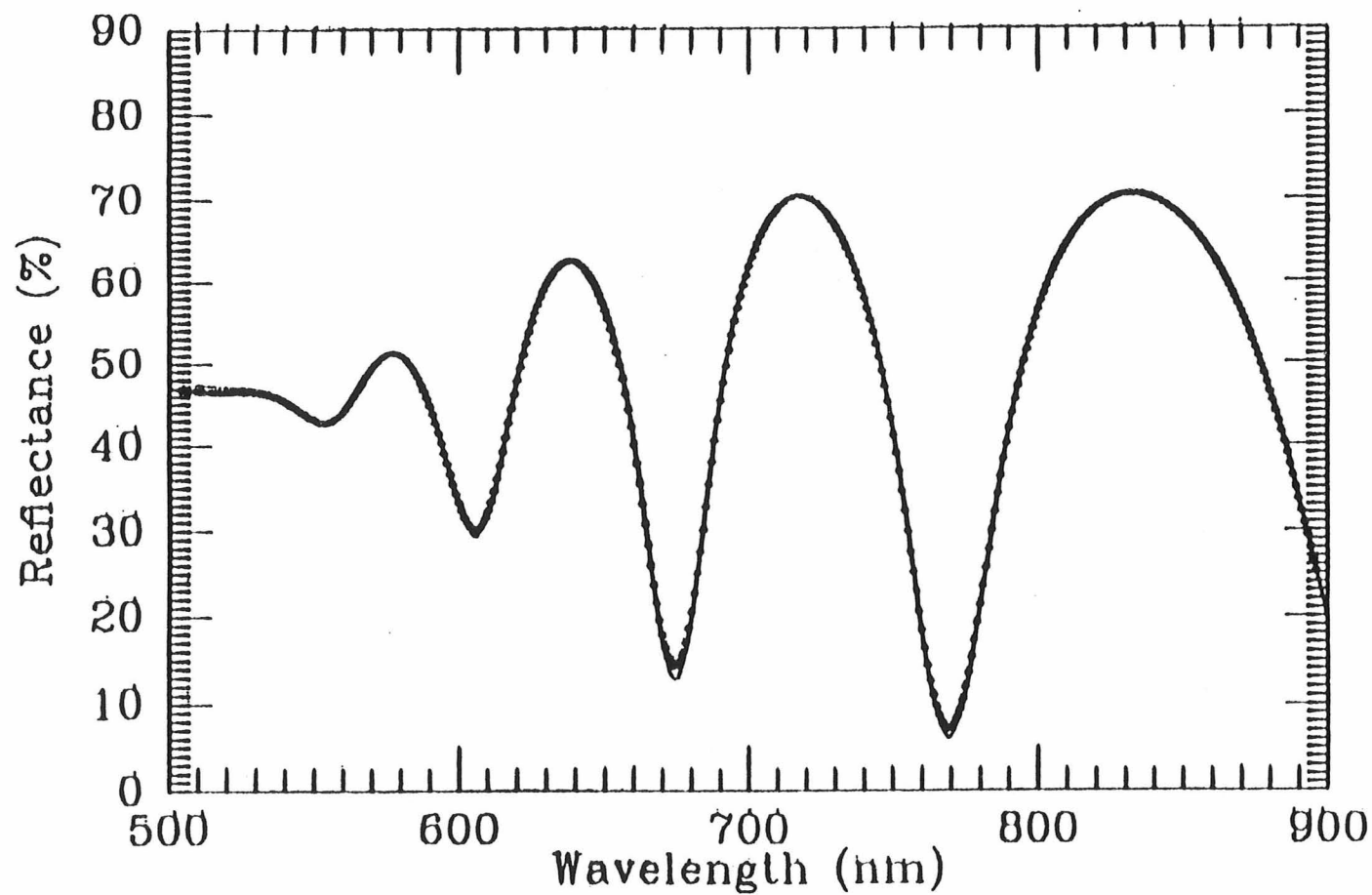


Fig. 4.8 (b) Simulated reflectance for a slit width of 4nm (dotted curve) compared to that of zero slit width (full curve) for a silicon film of 500nm thickness.

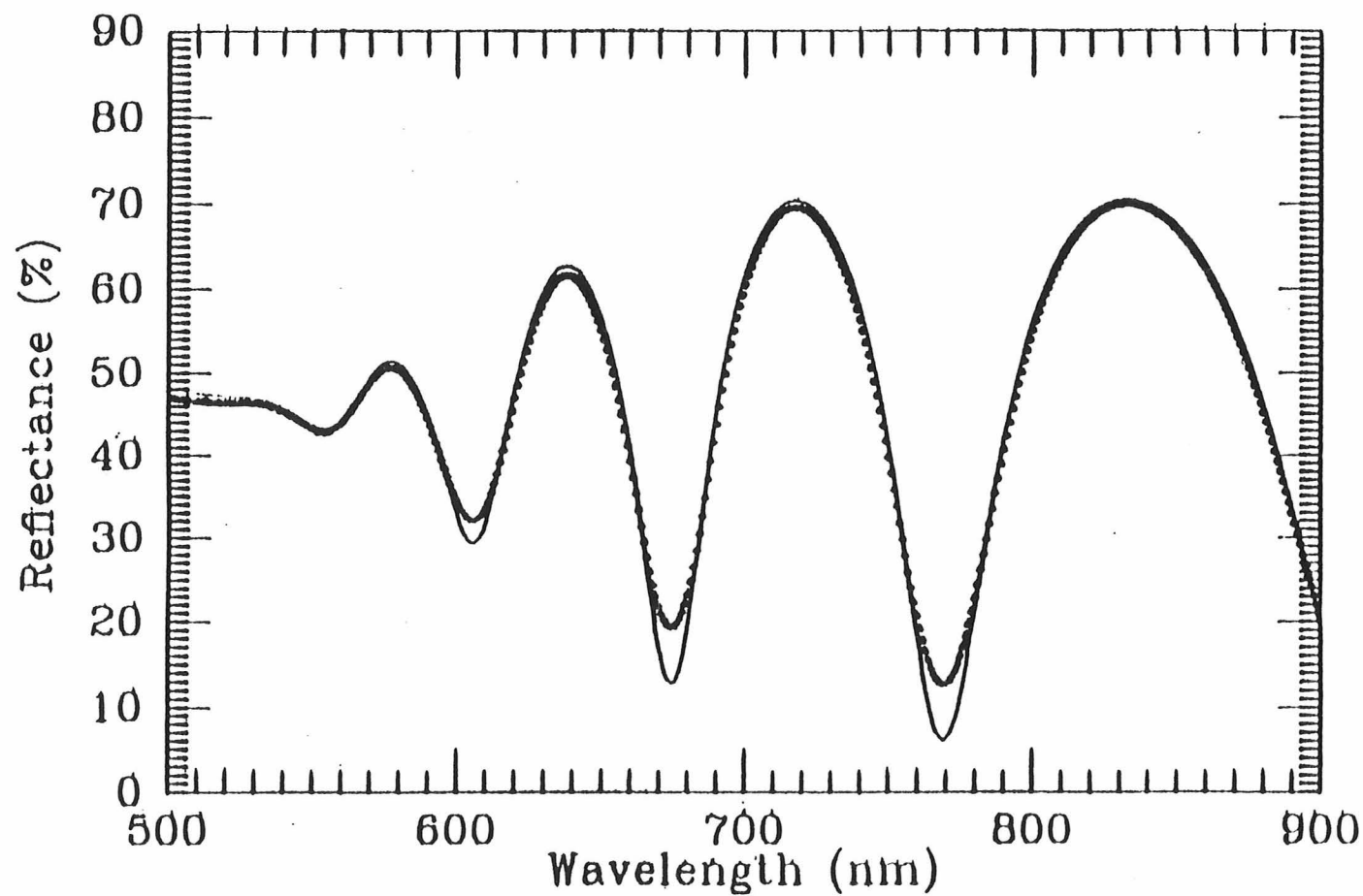


Fig. 4.9 Simulated reflectance for a silicon film of 500 ± 10 nm thickness (dotted curve) compared to that of a silicon film of exact 500 nm thickness (full curve).

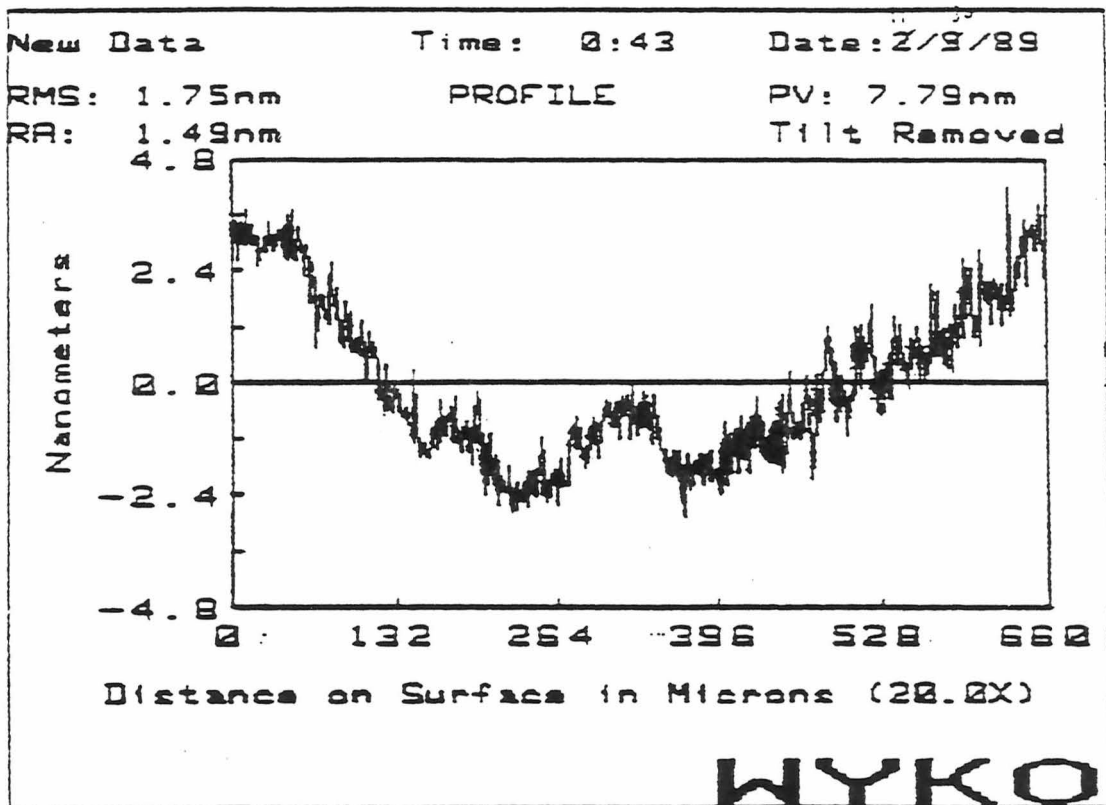


Fig. 4.10 Surface roughness of the boron thin film.

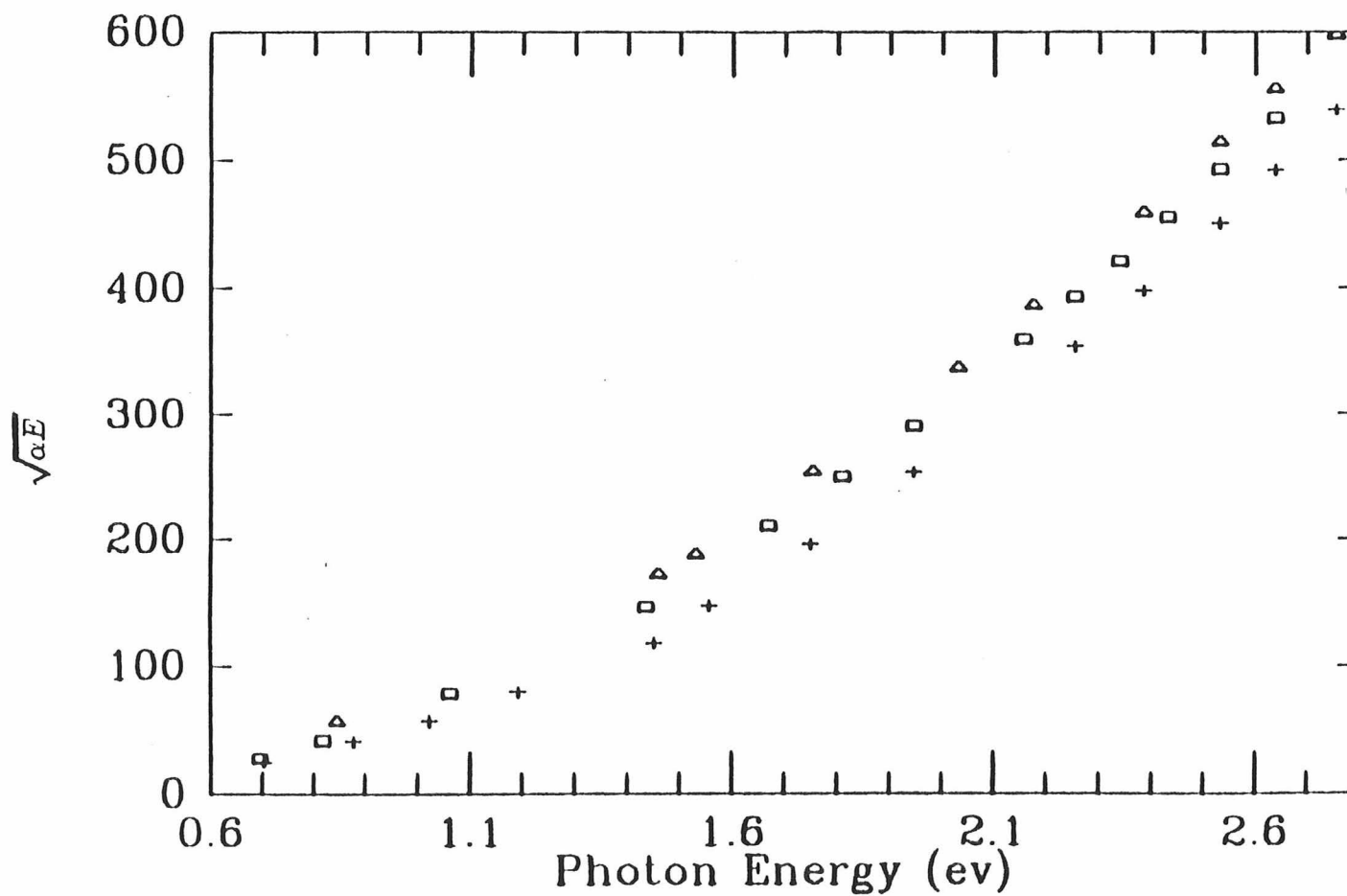


Fig. 4.11 Tauc plot of $(\alpha E)^{1/2}$ vs. E . The curve with signs + indicates the sample deposited at 2"; the curve with signs □ indicates the sample deposited at 3"; the curve with signs Δ indicates the sample deposited at 4".

V. MEASUREMENT OF THE RESISTANCE VS. TEMPERATURE

5.1 Model of Resistance for Amorphous Semiconductors

The temperature dependence of the electrical conductivity σ , or the electrical resistivity, $\rho = \frac{1}{\sigma}$, is one of the simplest to measure and most informative electrical properties of solid semiconductors. According to the Davis and Mott model³⁶ there is a relatively high density of localized states in the energy gap just as indicated in Fig. 5.1. Thus, for amorphous semiconductors three mechanisms of electrical conduction can be distinguished as follows:

1) Conduction due to carriers excited into non-localized or extended states. If the main current is carried by electrons we can expect, using the notation³⁶ of Fig. 5.1, that

$$\sigma = \sigma_0 \exp\{-(E_C - E_F)/kT\}, \quad (5.1)$$

where the constant σ_0 is a function of the coordination number, k is the Boltzmann constant, E_c and E_f are energies of the bottom of the conduction band and the Fermi energy level respectively. The difference between E_C and E_F is the activation energy for transport in non-localized states.

If the main current is carried by holes, the formula becomes:

$$\sigma = \sigma_0 \exp\{-(E_F - E_V)/kT\},$$

where E_V is the energy of the valence band and the other notations are same as above.

2) Hopping conduction due to carriers excited into the localized states at the band edge, i.e., E_A or E_B indicated in Fig. 5.2. If the main current is carried by electrons then

$$\sigma = \sigma_1 \exp\{-(E_A - E_F + \Delta W)/kT\}, \quad (5.2)$$

where ΔW is the activation energy for hopping and E_A is the energy at the band edge. An estimate of the constant σ_1 is not easy to make, but it is expected to be a factor of $10^2 \sim 10^4$ less than σ_0 .

If the main current is carried by holes then

$$\sigma = \sigma_1 \exp\{-(E_F - E_B + \Delta W)/kT\},$$

where E_B is the energy at the band edge.

3) Conduction due to carriers hopping (by tunnelling) between localized states near the Fermi energy. Then,

$$\sigma = \sigma_2 \exp\{A/T^{\frac{1}{4}}\}, \quad (5.3)$$

where σ_2 and A are constants.

5.2 Experimental Design, Procedure and Data Processing

The device I made for measuring resistance vs. temperature consists of the following:

- (1) a vacuum system with a copper case inside.

The case has four resistance coils and a passage for liquid nitrogen inside its walls so that it can be heated or cooled. The vacuum system can prevent

oxidation of the sample and the copper case while they are heated. The structure is shown in Fig. 5.3.

- (2) a four-point probe which can stand high temperature. This is not available commercially.

Fig. 5.4 indicates the structure of the probe. The circuit diagram of the whole system is shown in Fig. 5.5.

Boron thin films were deposited on Corning 7059 glass substrates as the samples of this experiment.

The experimental procedure is as follows:

- 1) Evacuate the whole system and, since light can generate electrical carriers in semiconductors, cover the bell jar with a piece of black cloth so that external light will not influence the sample, and consequently the electrical measurements.
- 2) Set a certain temperature and wait until the system is in thermal equilibrium.
- 3) Read out the current I_i from electrometer A and the voltage V_i from the electrometer B.
- 4) Set another temperature and repeat the above steps.
- 5) Calculate the sheet resistance at each temperature.

$$R_s = \frac{\rho}{d} = \frac{V_i}{R_i} C,$$

where ρ indicates the resistivity, d the thickness of the film. C is a constant dependant on the shape of the sample³⁷.

- 6) Make plots of $\ln \frac{1}{R_s}$ versus $\frac{1}{T}$ and versus $\frac{1}{T^{1/4}}$.

From equation (5.1) and (5.2) we can get

$$\ln \frac{1}{R_s} = \ln \frac{d}{\rho} = \ln d - \frac{a}{T} + b,$$

where b is a constant; a multiplied by the Boltzmann constant k is the activation energy for transport in the non-localized states. A plot of $\ln \frac{1}{R_s}$ against $\frac{1}{T}$ can be drawn. At low temperature it is appropriate to use Equation (5.3). The data which present a curve in the above plot will become a straight line in the plot of $\ln \frac{1}{R_s}$ against $\frac{1}{T^{1/4}}$ since Equation (5.3) can be written as

$$\ln \frac{1}{R_s} = \ln d - \frac{a'}{T^{1/4}} + b',$$

where a' and b' are constants.

5.3 Results and Discussion

Fig. 5.6 is the plot of $\ln \frac{1}{R_s}$ against $\frac{1}{T}$. Fig. 5.7 is the plot of $\ln \frac{1}{R_s}$ against $\frac{1}{T^{1/4}}$ for the low temperature data in Fig. 5.6. The three curves on both figures indicate the three kinds of samples mentioned above, i.e., they have the same hydrogen contents as the sample listed above. From Fig. 5.6 the three plots have three regions respectively: two are straight lines (one is above around 420°C, the other is between around 350°C and 420°C), the other is a curve ($T_{room} < T < 350^\circ\text{C}$), which indicates there are three mechanisms of electron transport. The data points on each of the plots in Fig. 5.7 roughly fall on a straight line. Thus I conclude that, generally, this is what is seen in other amorphous

semiconductors. The transportation of carriers in these samples is typical for amorphous semiconductors.

From the slope of the straight line in the high temperature region in Fig. 5.6 the activation energy of the sample can be found (see (5.1)). The following table summarizes what we found:

Table 5

location	constituent	resistivity at	activation	optical energy	
		room temperature			$\frac{E_{act}}{E_{opt}}$
(inch)	expression	(Ω -cm)	energy (eV)	gap (eV)	
2	$B_{0.56}H_{0.43}$	4.04×10^4	0.605	1.36	0.45
3	$B_{0.45}H_{0.55}$	9.13×10^3	0.572	1.18	0.49
4	$B_{0.33}H_{0.67}$	2.96×10^3	0.510	1.09	0.47

The above table shows that the resistivity of the amorphous boron at room temperature is quite large compared with crystalline semiconductors. The hydrogen content will influence the resistivity, activation energy and gap energy.

The above table also shows that the activation energies are almost half of the corresponding energy gaps which are measured from the Tau ϵ plots. This suggests the Fermi energy level is pinned in the midgap. This is in agreement with Davis and Mott's model³⁶ of amorphous semiconductors.

Since it is very hard to measure the exact thickness of the film, the plot of natural logarithm of conductivity versus temperature is not made. The data of

the resistivity in the table are measured from the samples of which the coating thicknesses were found by the optical method. Some of these samples were sent elsewhere for other optical measurements.

The measurement got from the four-point probe made by Megnetron Instrument Co. shows the a-B:H film is n type. This is the same type as pure a-Si:H films³⁸, but very different from crystalline boron which is p type.

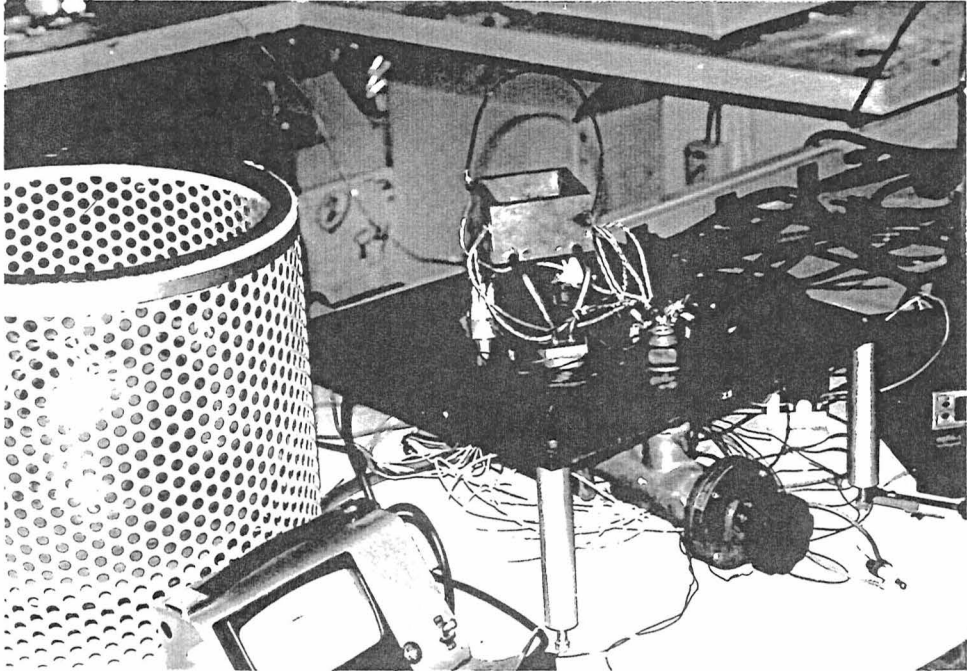


Fig. 5.3 Inside structure of the vacuum bell jar.

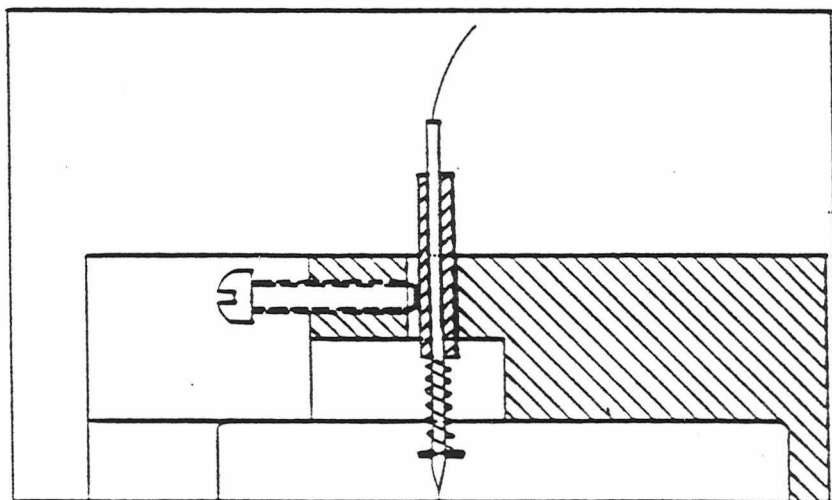
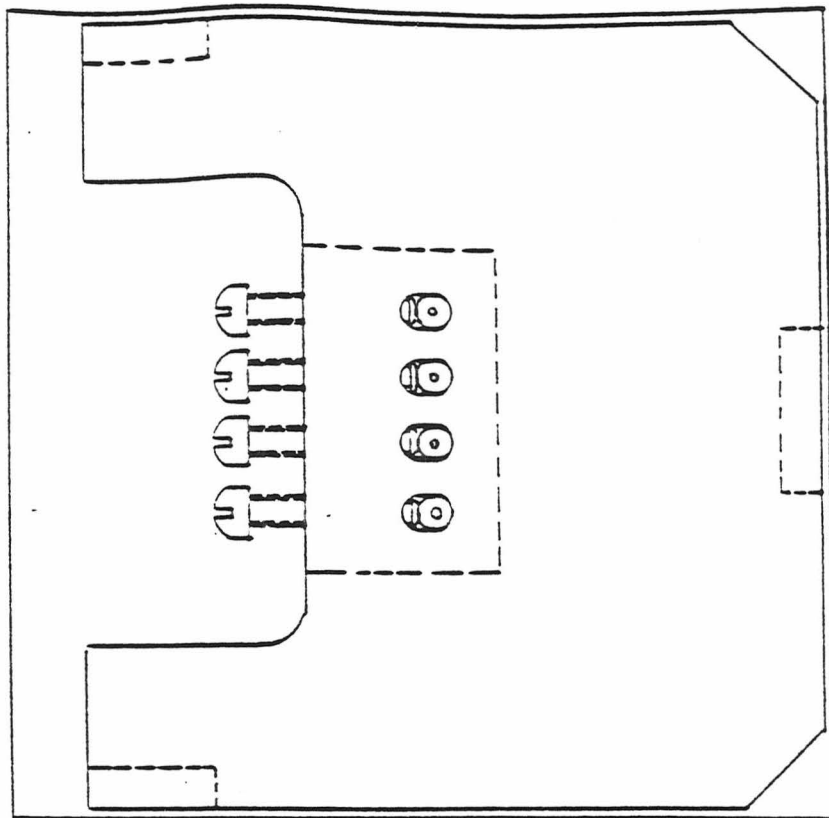


Fig. 5.4 Schematic diagram of the four-point probe.

Keithley 610C Electrometer

measuring voltage

current source

Keithley 610C

Electrometer

measuring current

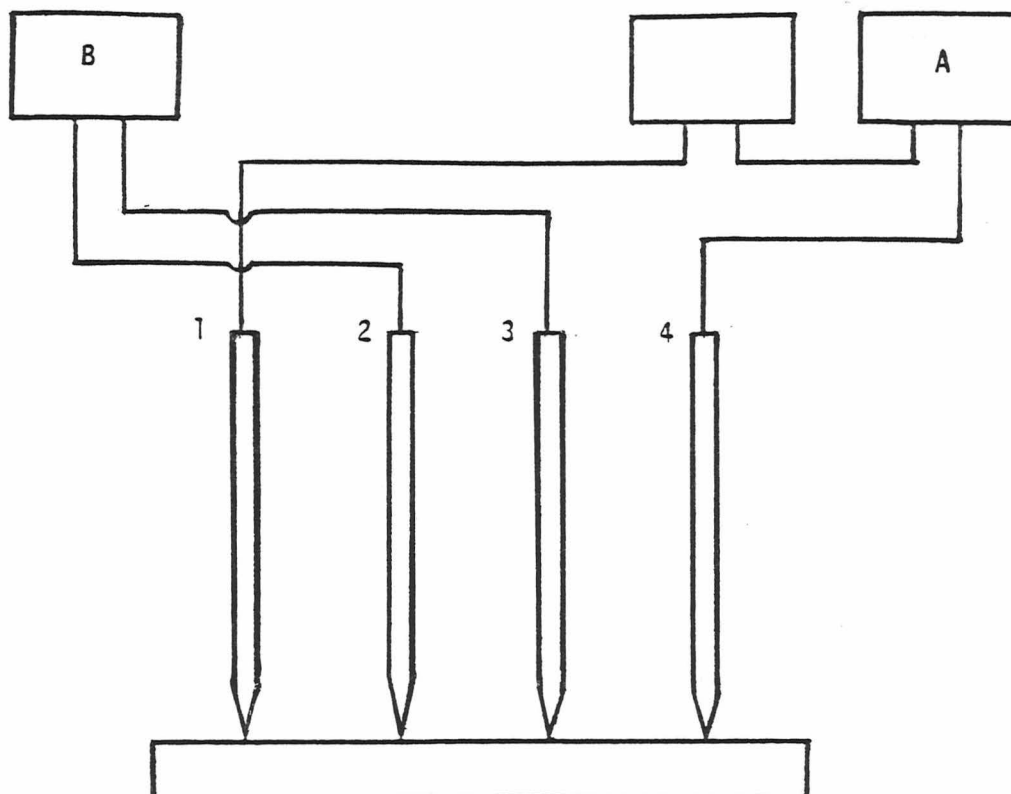


Fig. 5.5 Circuit diagram of the four-point probe.

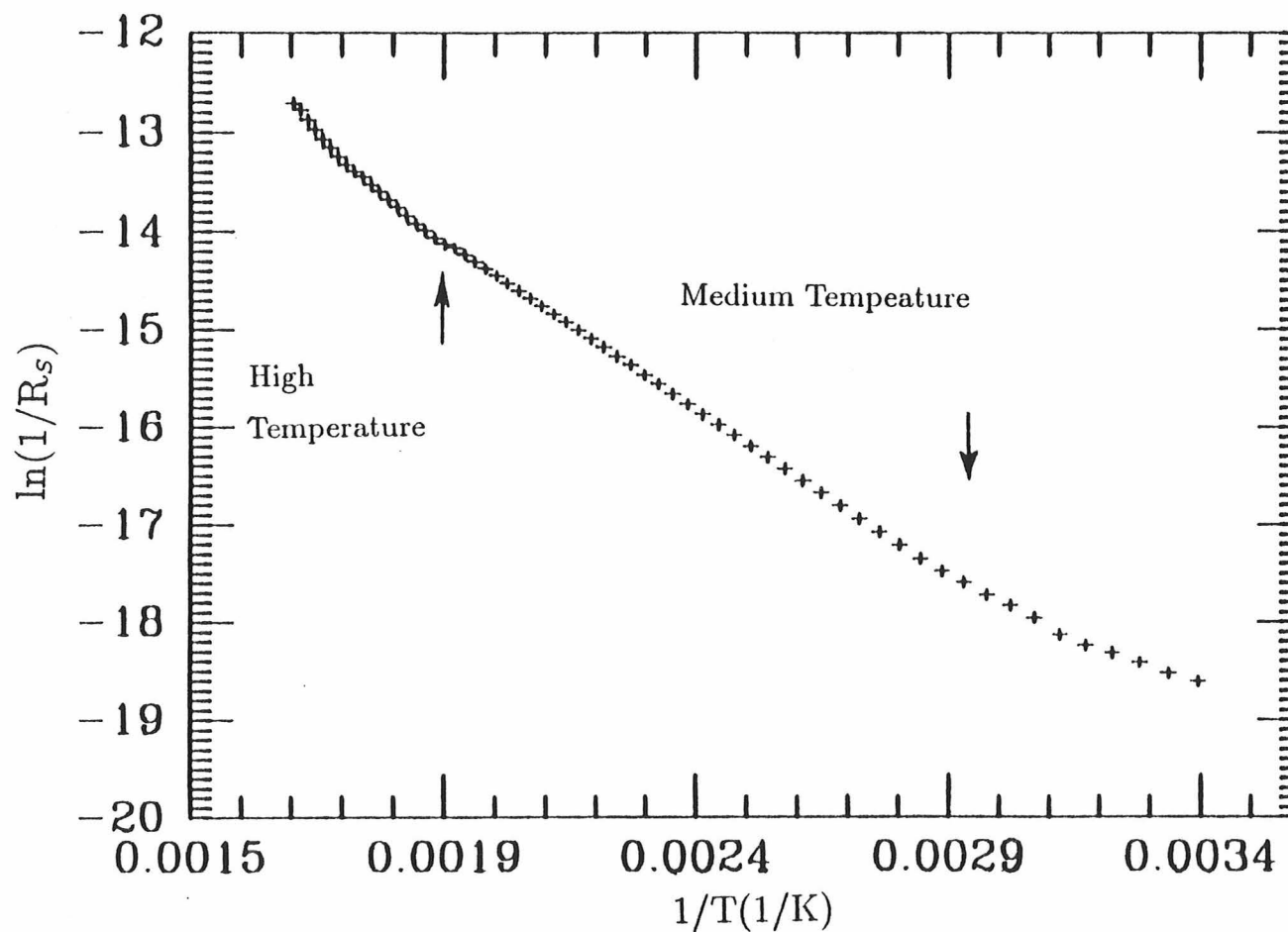


Fig. 5.6 (a). The plot of $\ln(1/R_s)$ against $1/T$ ($1/k$) for the boron film deposited at 2 inches from the entrance.

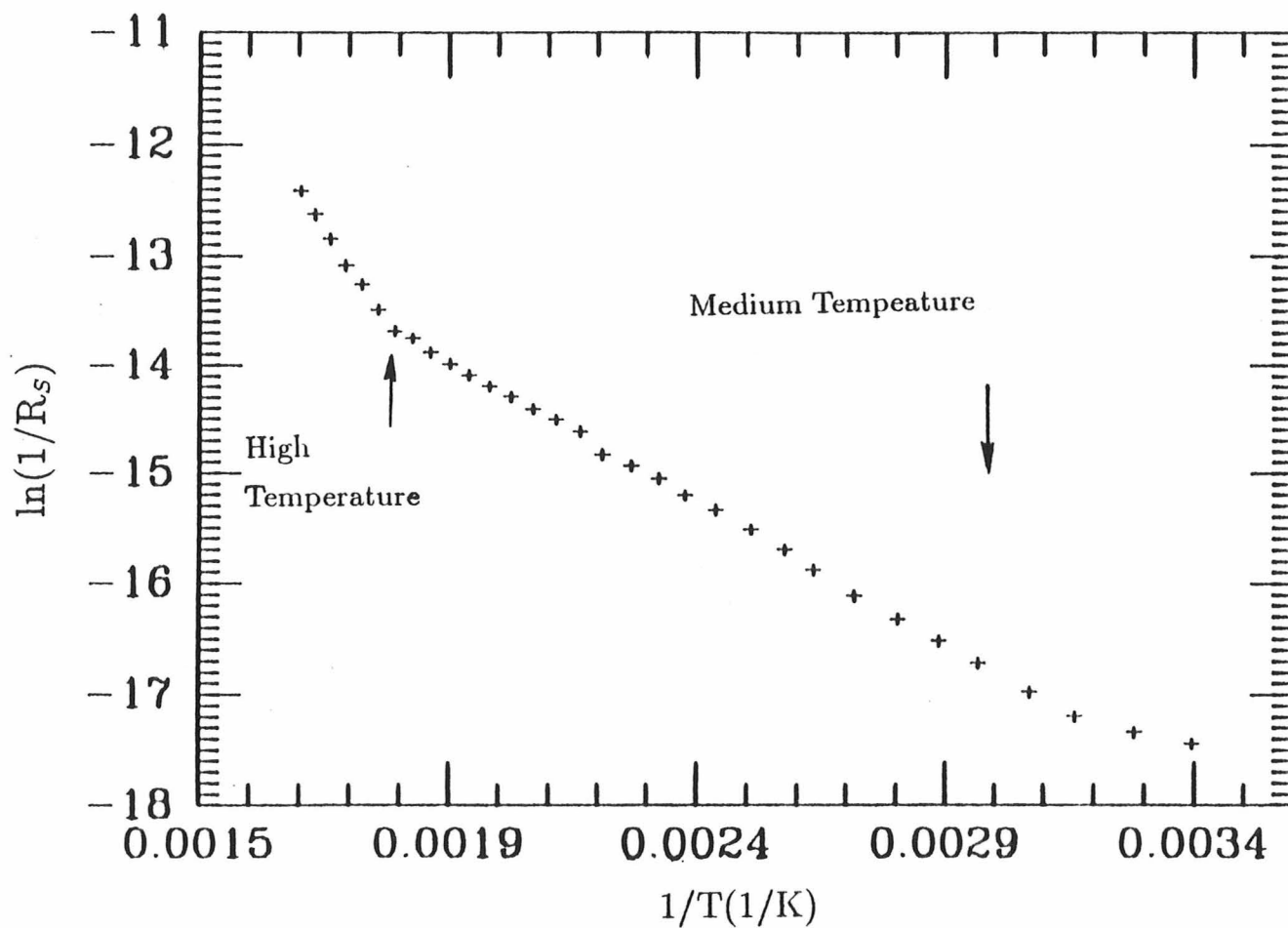


Fig. 5.6 (b) The plot of $\ln(1/R_s)$ against $1/T$ ($1/k$) for the boron film deposited at 3 inches from the entrance.

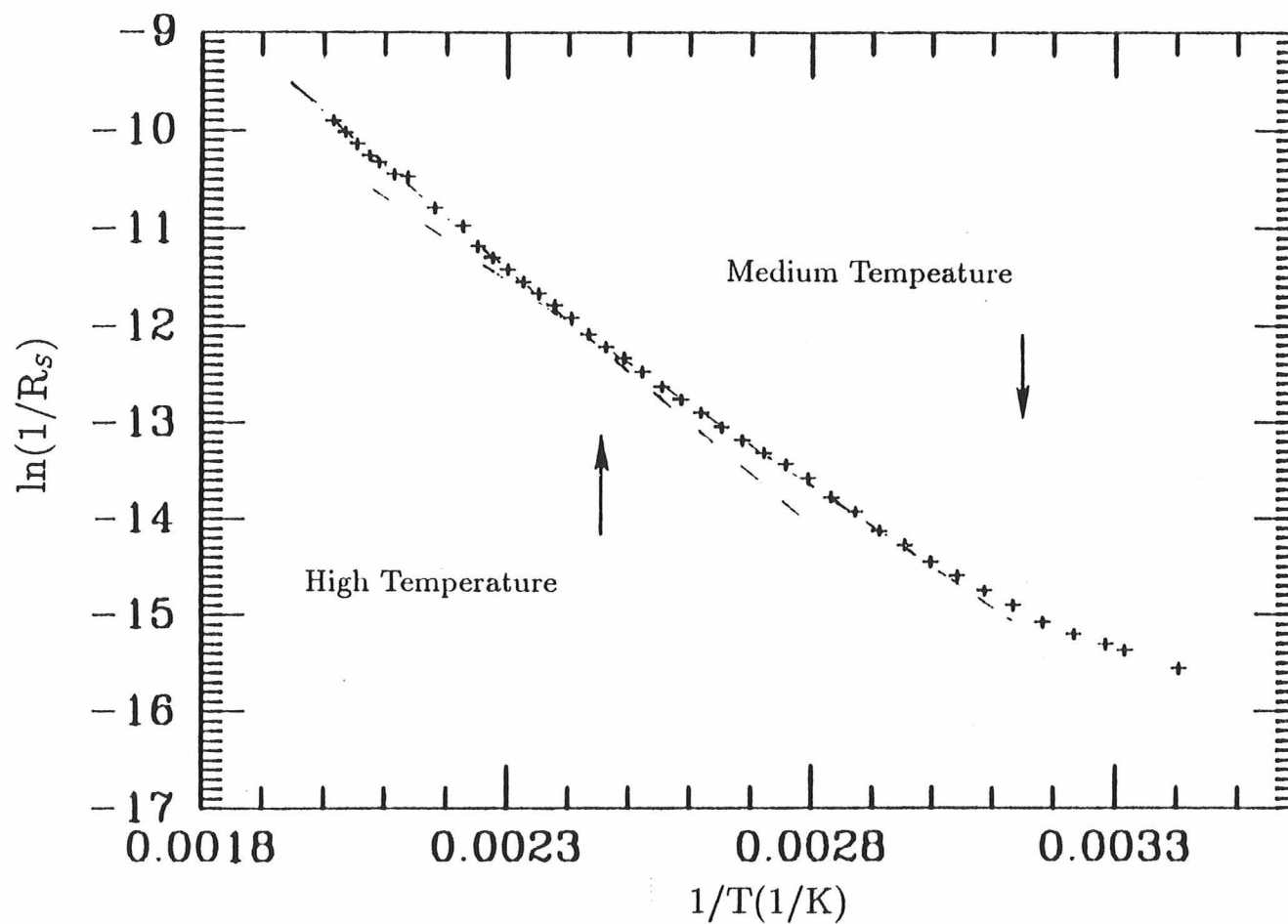


Fig. 5.6(c) . The plot of $\ln(1/R_s)$ against $1/T$ ($1/k$) for the boron film deposited at 4 inches from the entrance.

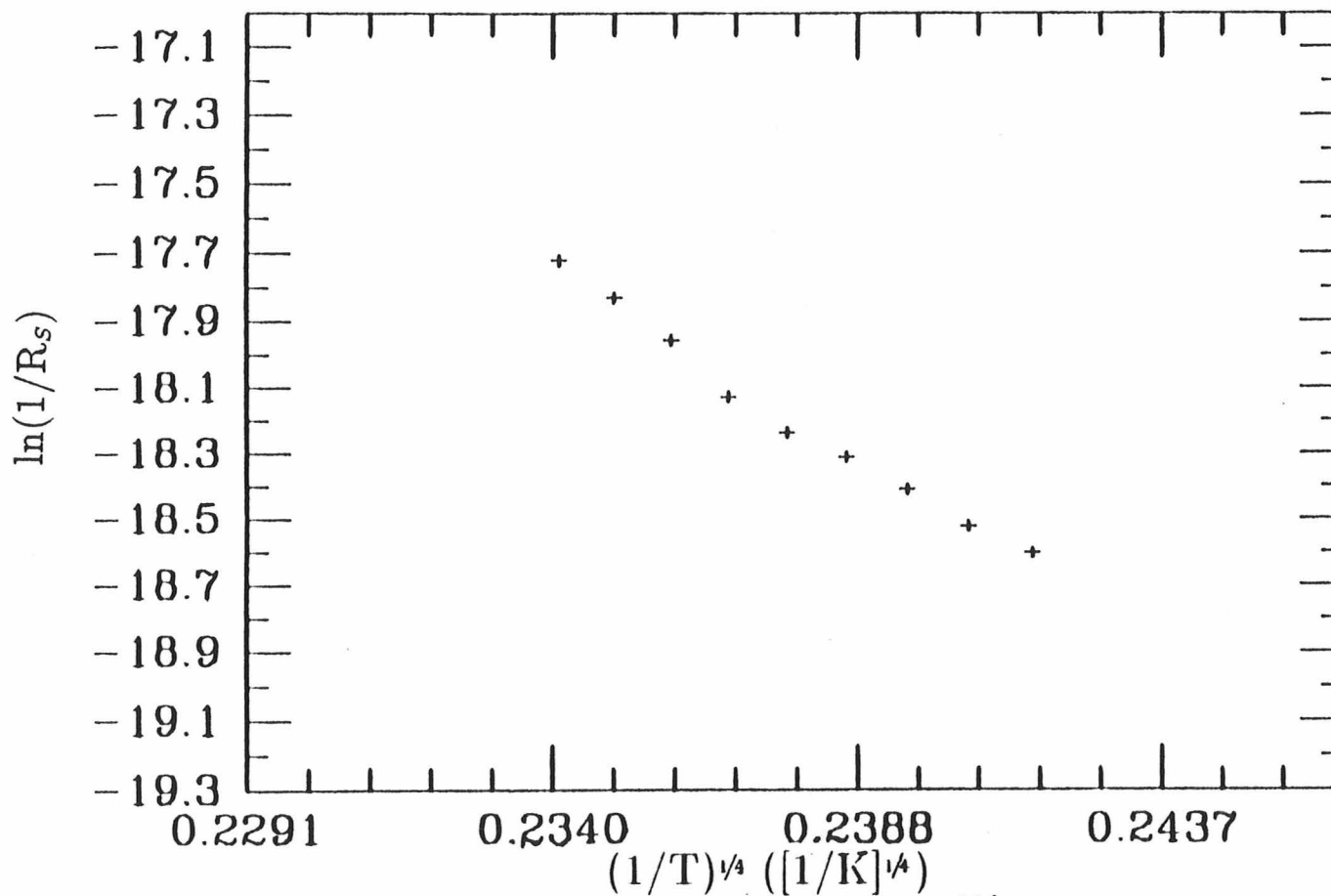


Fig. 5.7(a) The plot of $\ln(1/R_s)$ against $(1/T)^{1/4}$ for the boron film deposited at 2 inches from the entrance.

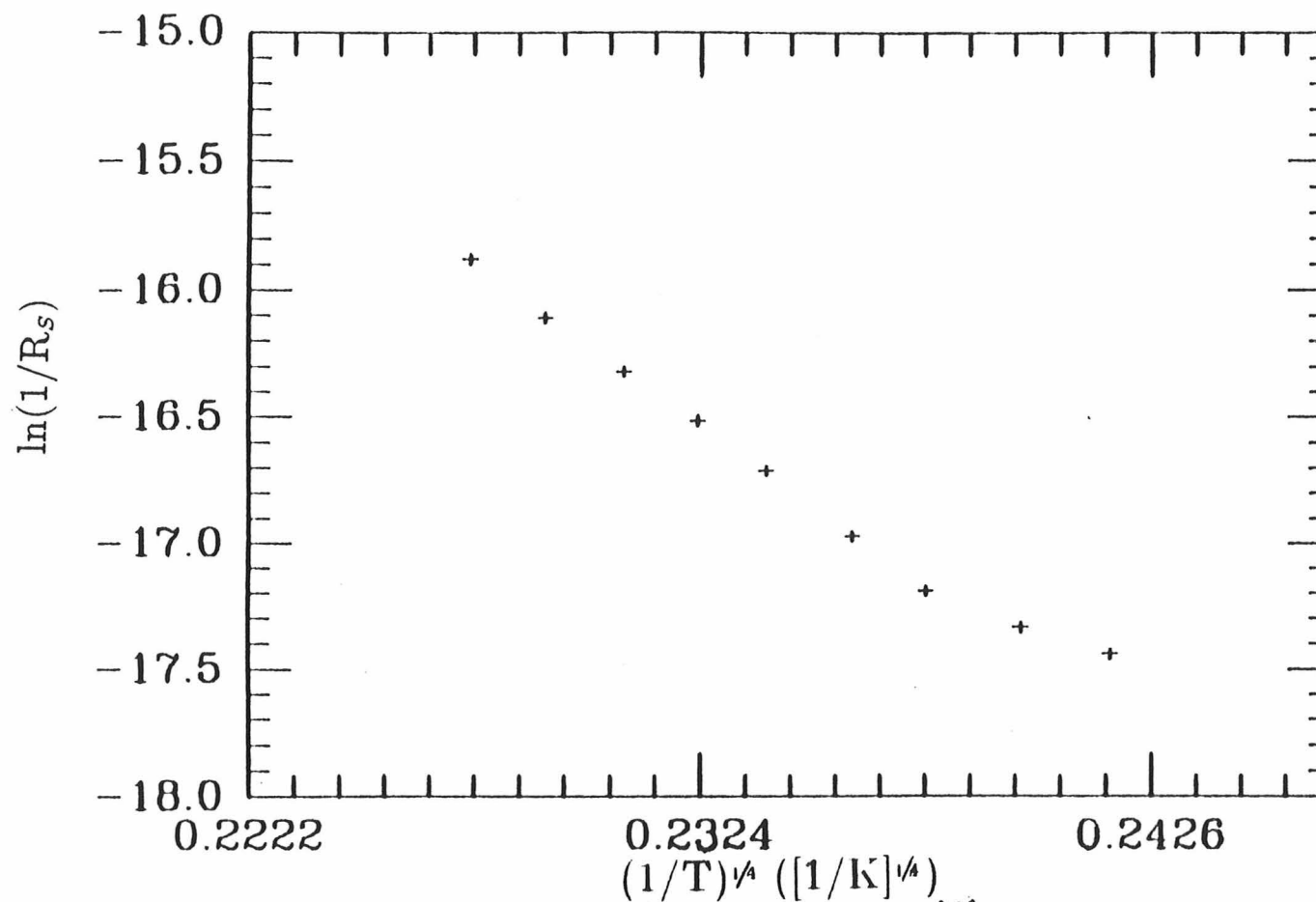


Fig. 5.7(b) The plot of $\ln(1/R_s)$ against $(1/T)^{1/4}$ for the boron film deposited at 3 inches from the entrance.

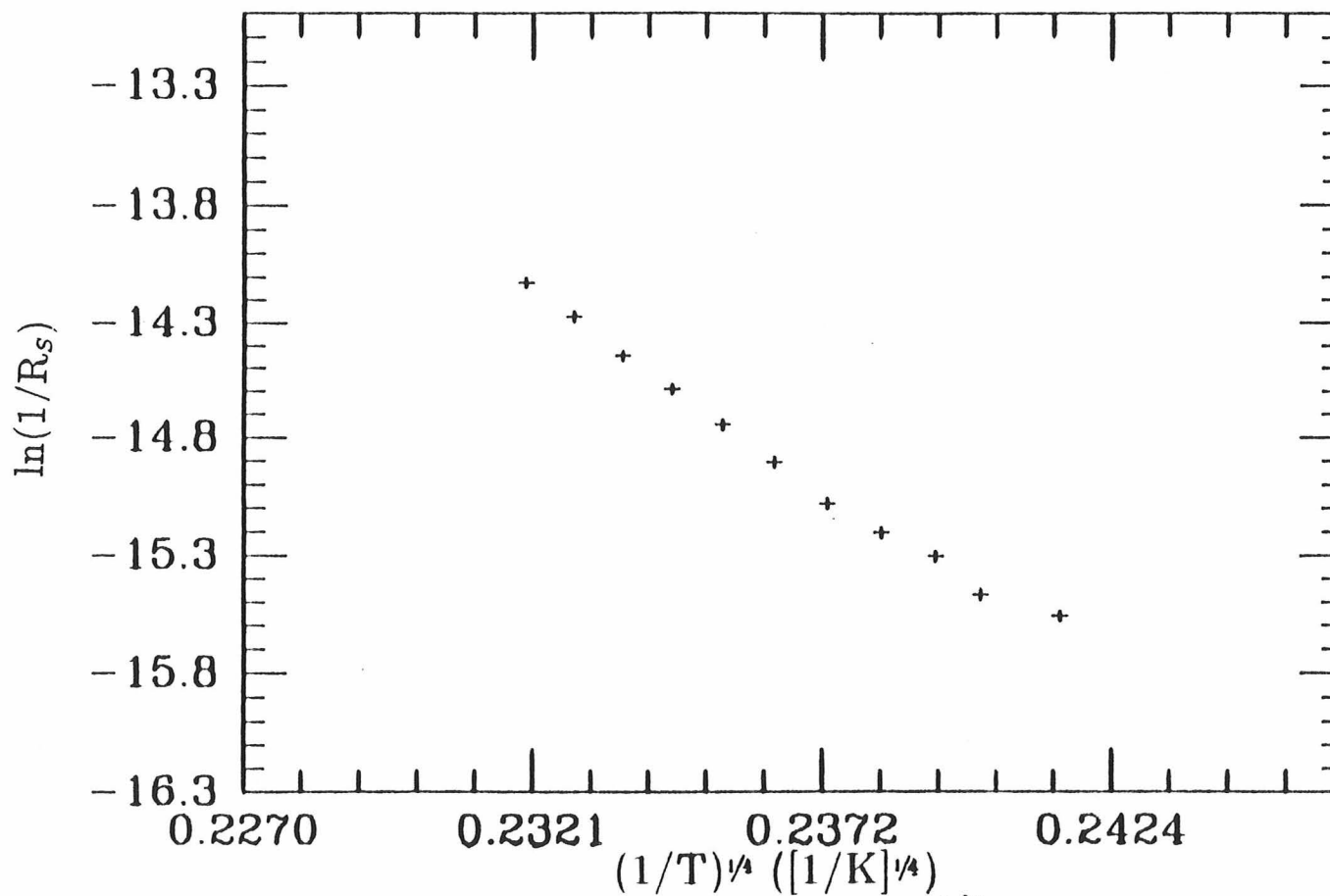


Fig. 5.7(c) The plot of $\ln(1/R_s)$ against $(1/T)^{1/4}$ for the boron film deposited at 4 inches from the entrance.

VI. MEASUREMENT OF MECHANICAL PROPERTIES OF BORON FILM

6.1 Introduction

The soft x-ray applications of boron film are closely related to its mechanical properties, i.e. its Young's modulus, its stress when boron films deposit on silicon wafers by low temperature CVD and its hardness. Thin film stress, usually a problem for integrated circuit processing, is being investigated as a potentially useful method of preparing figured x-ray optical elements. In my work chemical vapor deposited boron thin films are used to control bending silicon wafers with (110) surface orientation into cylindrical shapes. A model is proposed to describe and predict the bending of the boron/silicon structure. From this model the intrinsic stress and Young's modulus of boron coatings can be determined. The hardness of the boron films determines how resistive they are to the effect of abrasion.

In the following section of this chapter, the model and the measurement of stress and Young's modulus of boron films will be discussed. Section 3 focuses on the measurement of its hardness.

6.2 Measurement of the Young's Modulus and the Intrinsic Stress of the Boron Films on Silicon Wafers

6.2.1 Modeling of the Boron/Silicon Structure

The boron/silicon structure here refers to the sample of (110) silicon wafer coated with a thin film of boron on one side. Since we know the compliance of

silicon we can find the stress and Young's modulus of boron films by measuring the radius of curvature of the bent boron/silicon structure.

As we know the stress-strain relationship for any material in an arbitrary coordinate system $x'y'z'$ is as follows:

$$\epsilon'_{ij} = s'_{ijkl} \sigma'_{kl}, \quad i,j,k,l=1,2,3$$

where ϵ' and σ' are the strain and stress respectively, s' is the elastic compliance constant. Symmetry considerations³⁹ indicate that each of the stress and strain tensors has 6 independent elements while the compliance tensor, s' , has 36. Thus the stress-strain relationship in matrix form can be written as follows:

$$\epsilon'_i = s'_{ij} \sigma'_j, \quad i,j=1,2,\dots,6$$

The subscripts in the above two forms of the stress-strain relationship have the following correspondence,

$$11 \rightarrow 1, \quad 22 \rightarrow 2, \quad 33 \rightarrow 3,$$

$$23, 32 \rightarrow 4, \quad 31, 13 \rightarrow 5, \quad 12, 21 \rightarrow 6.$$

If we set up the coordinate system $x'y'z'$ indicated in Fig. 6.1, the absence of shear stress in the boron/silicon structure gives⁴³

$$\sigma'_4 = \sigma'_5 = \sigma'_6 = 0$$

$$\epsilon'_4 = \epsilon'_5 = \epsilon'_6 = 0$$

The lack of constraints in x' direction reduced σ'_1 to zero. Then $\vec{\sigma}'$ becomes

$$\vec{\sigma}' = (0, \sigma'_2, \sigma'_3, 0, 0, 0).$$

Thus the stress-strain relationship can be simplified as

$$\epsilon'_i = s'_{ij} \sigma'_j, \quad i=1,2,3; j=2,3$$

so that for the structure modeling there exist the following basic equations of the stress-strain relationship:

$$\begin{aligned} \epsilon'_3 &= s'_{32} \sigma'_2 + s'_{33} \sigma'_3 \\ \epsilon'_2 &= s'_{22} \sigma'_2 + s'_{23} \sigma'_3 \end{aligned} \tag{6.1}$$

The transformation in Fig. 6.1 from the crystal axes x_i (unprimed) to the arbitrary system x'_i (primed) is described by

$$x'_i = l_i x_1 + m_i x_2 + n_i x_3, \quad i=1,2,3$$

where l, m, n are the directional cosines of the transformation.

According to Worthman⁴⁰, in order to calculate the coefficients for an arbitrary rectangular system (rotated axes), one must perform a transformation. The results of such a transformation are shown as follows:

$$s'_{33} = s_{11} + s_c(l_3^4 + m_3^4 + n_3^4 - 1)$$

$$s'_{22} = s_{11} + s_c(l_2^4 + m_2^4 + n_2^4 - 1)$$

$$s'_{23} = s_{12} + s_c(l_2^2 l_3^2 + m_2^2 m_3^2 + n_2^2 n_3^2)$$

where

$$s_c = s_{11} - s_{12} - \frac{1}{2}s_{44}.$$

Since for crystal silicon^{40,41}

$$s_{11} = 0.768 \times 10^{-12} \text{ cm}^2/\text{dyn},$$

$$s_{12} = -0.214 \times 10^{-12} \text{ cm}^2/\text{dyn},$$

$$s_{44} = 1.26 \times 10^{-12} \text{ cm}^2/\text{dyn},$$

we can get

$$s'_{33} = 0.768 \times 10^{-12} \text{ cm}^2/\text{dyn},$$

$$s'_{22} = 0.592 \times 10^{-12} \text{ cm}^2/\text{dyn},$$

$$s'_{23} = s'_{32} = -0.214 \times 10^{-12} \text{ cm}^2/\text{dyn}.$$

Fig. 6.1(e) shows the general feature of the curving of the silicon wafer described by the set of basic equations in (6.1). The extreme wafer strains appear along z' and y' directions. There is no shear strain involved in the curving.

It is noted that in the boron film on a silicon wafer the stress mentioned here is the intrinsic stress, not the equilibrium stress. The intrinsic stress is the equilibrium stress when the silicon wafer is rigid. When equilibrium in the structure is reached, a thin film under stress will curve its substrate relaxing some of its the stress which strains the substrate. This implies that for different

film/substrate structures the stress relaxation in the film will be different. Thus the equilibrium stress in the films is in general different from sample to sample. The intrinsic stress of the film, however, stays the same. The following σ_{in} will be indicated as the intrinsic stress in boron film on silicon wafers.

It is useful to imagine that the curving of the structure is achieved in two steps. In the first step the structure remains flat until the deposition of the boron film is completed (see Fig. 6.2(b)). Then, a contraction occurs while the structure remains flat (see Fig. 6.2(c)). The first step continues until the sum of forces across the cross section is zero. Then curving of the structure occurs to counterbalance the moments induced by contraction. The second step ends when the sum of moments across the cross section is zero (see Fig. 6.2(e)).

It is also assumed that there is a sharp boundary between boron and silicon. This is very reasonable. As we know, the diffusion coefficient is given by $D = D_0 \exp(-E/kT)$, where $D_0 = 0.76 \text{ cm}^2/\text{s}$, and $E = 3.46 \text{ eV}$ for boron⁴² in silicon. Thus, for the deposition temperature $T = 450^\circ\text{C}$, D is very small, i.e., $D \sim 10^{-25} \text{ cm}^2/\text{s}$. The deposition time for very thin boron film is short (about 3000 seconds). Since the characteristic diffusion distance is thus about 10^{-11} cm , which is considerably less than one interatomic distance (10^{-8} cm), the assumption that there is an abrupt interface is correct.

Let E_f and E_s be the Young's moduli of boron films and silicon substrates, respectively. Before the structure contraction occurs the film is under its highest

tension, i.e., the intrinsic stress, and the substrate is free of stress. The contraction of the structure starts, partially releasing the tension in the film and building up compressive stress in the substrate until the force of compression in the substrate equals the force of tension in the film. Let that strain of contraction be δ at that point. Thus, the tension in the film is given by: $\sigma' = \sigma_{in} - E_f \delta$, and the compressive stress in the substrate σ'' becomes $E_s \delta$. The summation of forces should be zero, i.e.,

$$\sigma'' t_s = \sigma' t_f$$

From the above relationship we can get

$$\delta = \frac{\sigma_{in} t_f}{E_f t_f + E_s t_s}.$$

From Fig. 6.2(c), the tensile force in the film and the compressive force in the substrate set up a moment per unit width in the flat structure,

$$M_l = -\frac{\sigma_{in} t_f t_s E_s (t_s + t_f)}{2(E_s t_s + E_f t_f)}.$$

At equilibrium, the structure will take up additional strain and the associated stress (see Fig. 6.2(e) and (e)). Zero total forces and zero total moment over any cross section at equilibrium put two constraints on the stress.

The cross section of the bending structure is displayed in Fig. 6.3(a). Since the radius of curvature is large, we can approximate it as triangles indicated in Fig. 6.3(b). Using the properties of similar triangles we can find the strain as follows:

$$\epsilon = \frac{\Delta l}{l} = \frac{x}{r}. \quad (6.2)$$

Thus, from the first constraint we can get

$$E_s d = \frac{(t_s - d)^2}{d} E_s + \frac{t_f + 2t_s - 2d}{d} t_f E_f,$$

where d is the distance between the top surface and the neutral surface. Solving the above equation,

$$d = \frac{t_s}{2} + \frac{E_f t_f (t_s + t_f)}{2(E_s t_s + E_f t_f)}.$$

Now consider the second constraint on the stress in Fig. 6.2(d). The neutral point is taken as a pivot to find the moment of the whole system. Let M_1 be the moment from the stress in the substrate and M_2 be the moment from the stress in the film.

$$M_1 = \frac{E_s}{3r} [d^3 + (t_s - d)^3]$$

$$M_2 = \frac{E_f}{3r} [(t_s + t_f - d)^3 - (t_s - d)^3]$$

The total bending moment is as follows:

$$M_b = M_1 + M_2 = \frac{E_s [E_f (t_s + t_f)^4 + (E_s - E_f) (t_s^4 - \frac{E_f}{E_s} t_f^4)]}{12r (E_s t_s + E_f t_f)}$$

In this experiment $t_s \gg 50t_f$. Assume that E_f is of the same order of magnitude as E_s , then $(E_f/E_s)t_f^4$ is insignificant compared with t_s^4 and can be negligible.

Since the net bending moment should be zero, i.e., $M_b + M_l = 0$, we get

$$\frac{\sigma_{int_s} t_f E_s (t_s + t_f)}{2(E_s t_s + E_f t_f)} = \frac{E_s [E_f (t_s + t_f)^4 + (E_s - E_f) t_s^4]}{12r (E_s t_s + E_f t_f)}. \quad (6.3)$$

Before it could be of any use, all the E 's have to be determined. From (6.2)

we know that for the strain in z direction $\epsilon'_s = \frac{x}{r_s}$, and for strain in y direction

$\epsilon'_2 = \frac{x}{r_l}$. Substituting these into (6.1) we get

$$\epsilon'_3 = (s'_{33} + s'_{32} \frac{s'_{33} - Rs'_{32}}{Rs'_{22} - s'_{32}}) \sigma'_3 = s'_{equiv} \sigma'_3, \quad (6.4)$$

where $R = r_l/r_s$. When $R > 20$, the equivalent compliance is a constant⁴³. In our situation the bent structure is approximately cylindrical. Thus the above condition can be satisfied. Also (6.2) can be reduced further:

$$\sigma_{int} t_s t_f (t_s + t_f) = \frac{E_f (t_s + t_f)^4 + (E_s - E_f) t^4}{6r}, \quad (6.5)$$

where r indicates the radius of curvature in the z direction.

If we measure two groups of data such as t_f , t_s , r , we can set up two simulated equations like (6.4), so as to determine σ_{in} and E_f for both films.

6.2.2 Procedures and Results

Thin boron films were deposited on 2" diameter wafers with both sides polished and a thickness of $3 \text{ mil} \pm 0.3 \text{ mil}$. The deposition locations were the same for the two experiments. Different deposition times were used, however, so the thicknesses of the deposited films were different. The nominal deposition temperature was 450°C . After deposition the sample was left in the oven until it cooled down to room temperature. After deposition both original flat wafers became cylindrically bent. The minimum radius of curvature in the Z direction are as follows:

sample	t_f (in cm)	r (in cm)
1	5.789×10^{-5}	43.8
2	8.684×10^{-5}	34.9

Since $R = r_l/r_x > 20$, from (6.4) we can get

$$\epsilon'_3 = (s'_{33} - \frac{s'_{32}}{s'_{22}})\sigma'_3.$$

Thus $E_s = 1.448 \times 10^{12}$ dyn/cm². Solving two simultaneous equations like (6.5) we get $E_f =$

$$\frac{[Rt_{f1}(t_s + t_{f1}) - t_{f2}(t_s + t_{f2})]E_s t_s^4}{t_{f2}(t_s + t_{f2})[(t_s + t_{f2})[(t_s + t_{f1})^4 - t_s^4] - Rt_{f1}(t_s + t_{f1})[(t_s + t_{f2})^4 - t_s^4]} \quad (6.6)$$

Substituting the above data into (6.6) we get $E_f = 3.05 \times 10^{13}$ dyne/cm², $\sigma_{in} = 9.03 \times 10^9$ dyne/cm².

As we know, the silicon wafer of 3 mil thickness has 10% variation in thickness. We use a WYKO profilometer instrument to measure the radius of curvature and measure the thickness of the boron film by etching the film into a step. Assuming that the variation of film thickness is 3%, and error of the ratio of two radii of curvature is 2%, then from (6.6) we can find that the possible error of E_f is about 11%, i.e., E_f is $3.05 \times 10^{13} \pm 3.23 \times 10^{12}$ dyne/cm².

The Young's modulus of boron is larger than those of some other materials such as nickel. A 4 μ m boron film was deposited on a 3" diameter silicon wafer with a thickness of 0.5 mm. The surface of the silicon wafer broke because of the stress of the boron film when the sample was taken out of the hot oven. Parts of the silicon on the surface were stuck on the film and taken off so that an unusual pattern can be seen on the surface. (see Fig. 6.4)

Fig. 6.5 is a boron window with a thickness of about 1 μ m. After finishing boron deposition on the silicon wafer we took the sample out of the hot oven,

let it cool down rather than let it cool inside the evacuated quartz tube, then selectively etched the silicon away. The boron window possesses some ripples which indicates that the stress of boron is compressive relative to the silicon wafer. This contradicts the determination of tensile stress above. It seems that the process of cooling down the deposited boron films more naturally and gradually may change compressive stress to tensile stress or there may be something more. This subject needs to be studied further.

6.3 Measurement of Hardness for CVD Boron Film

Since we do not have capability to measure the hardness of material here, Dr. Randich of Lawrence Livermore National Lab was asked to help us.

He used a diamond indenter to measure the hardness of our boron films. The basic principle of that instrument is as follows⁴⁴:

A pyramidal diamond indenter is pressed into the surface of a film under a load of W kg and the mean diagonal of the resultant indentation is measured (d mm). The Vickers diamond hardness is defined as

$$Vdh = \frac{W}{\text{pyramidal area of indentation}}.$$

The indenter generally has an angle of 126° between opposite faces and 146° between opposite edges. From simple geometry, this means that the pyramidal area of the indentation is greater than the projected area of the indentation by the ratio 1:0.9272. Hence

$$Vdh = \frac{0.9272W}{\text{projected area of indentation}} = 1.8544W/d^2.$$

The value is expressed in kg/mm^2 .

Dr. Randich found that the hardness of the boron films is around 2500 Vickers when the loads ranging from 10 to 25 gram are used. Diamond, the hardest material, has a hardness of around 10000 Vickers⁴⁵. Most of low temperature deposited materials are not as hard as boron film. In addition, boron can withstand temperatures as high as above 600°C while diamond will become graphite at these temperatures. It can be expected that CVD boron films could be widely used in industry.

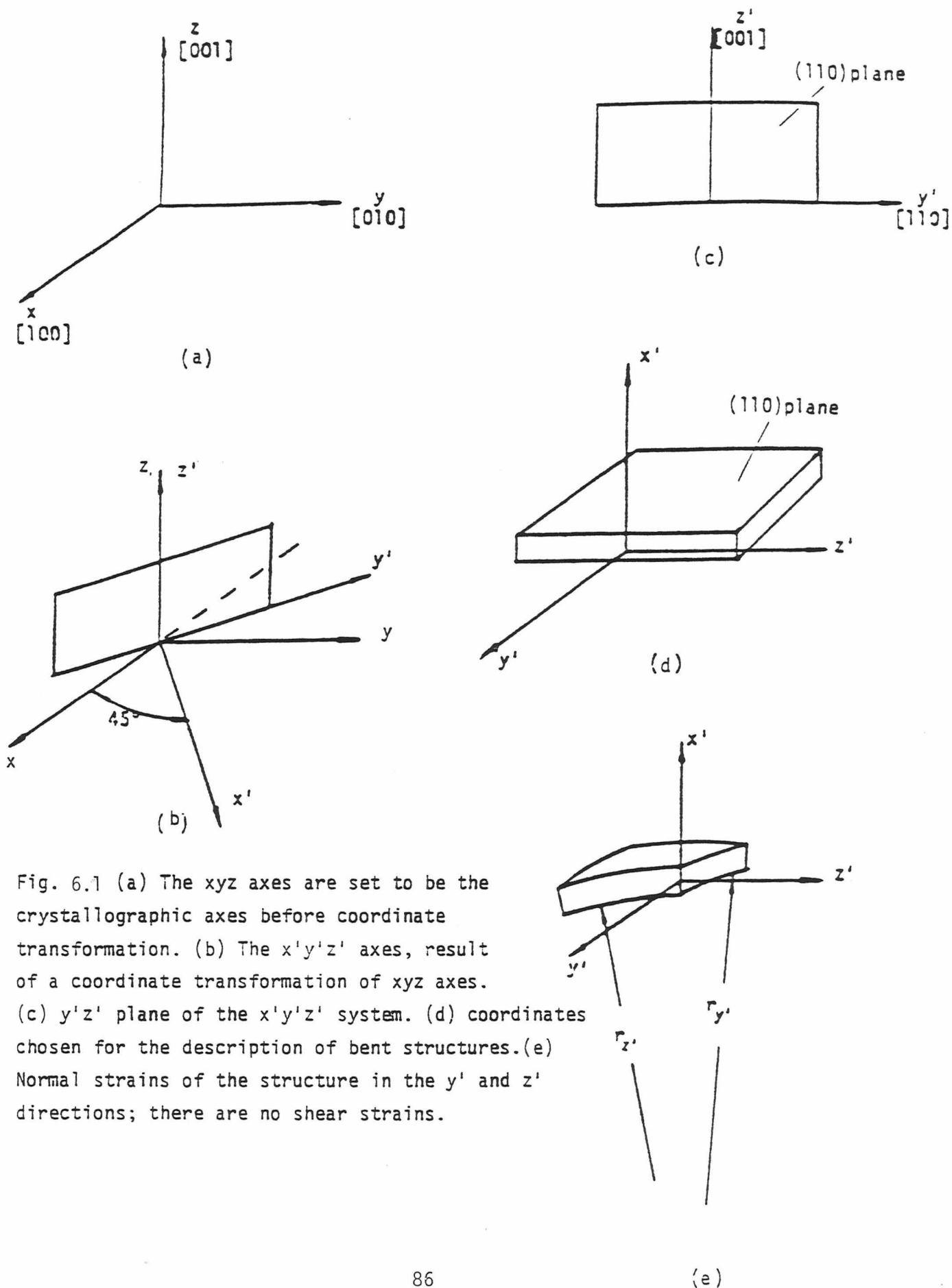


Fig. 6.1 (a) The xyz axes are set to be the crystallographic axes before coordinate transformation. (b) The $x'y'z'$ axes, result of a coordinate transformation of xyz axes. (c) $y'z'$ plane of the $x'y'z'$ system. (d) coordinates chosen for the description of bent structures. (e) Normal strains of the structure in the y' and z' directions; there are no shear strains.

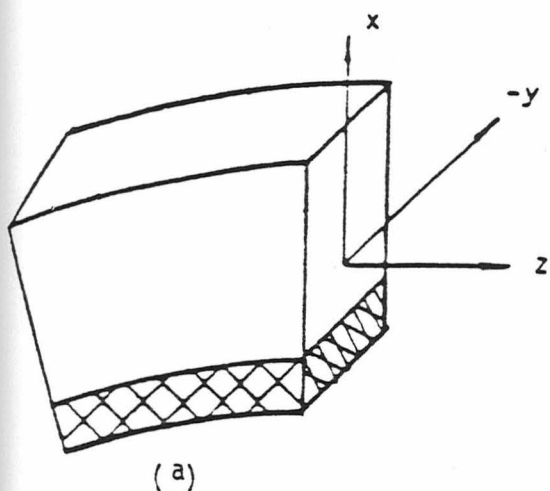
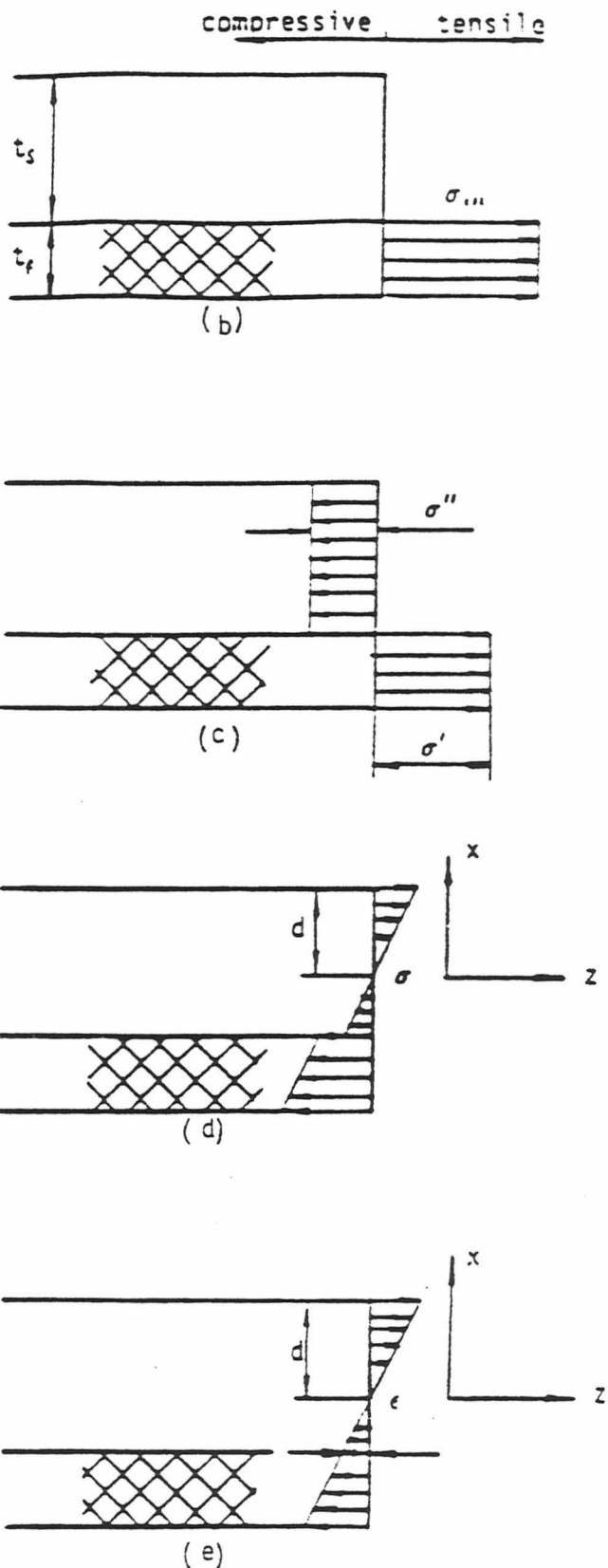


Fig. 6.2 (a) The bent substrate with a film coated. (b) The structure keeps flat when the deposition film is barely completed. (c) Contraction happens while the structure remains flat. (d) The stress distribution of the bent structure. (e) The strain distribution of the bent structure.



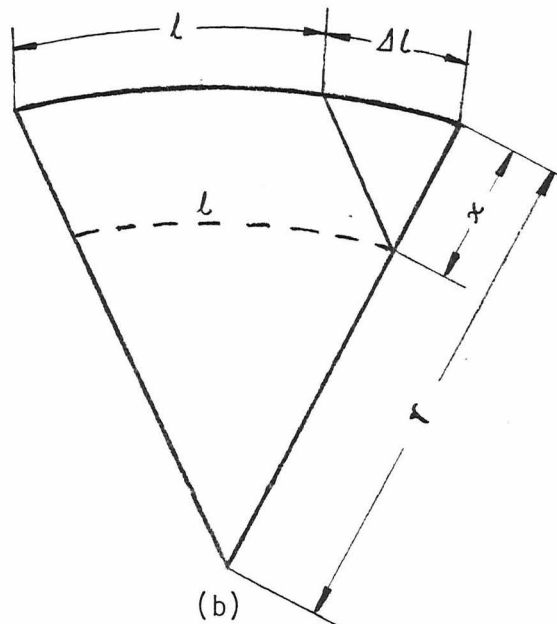
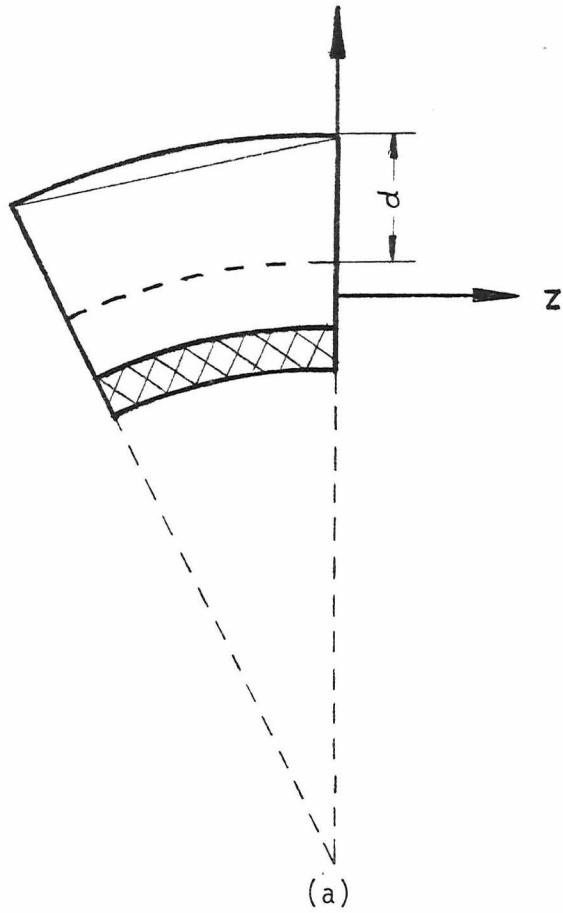


Fig. 6.3 (a) The cross section of the bent structure.
 (b) The triangle approximation for the bent structure.

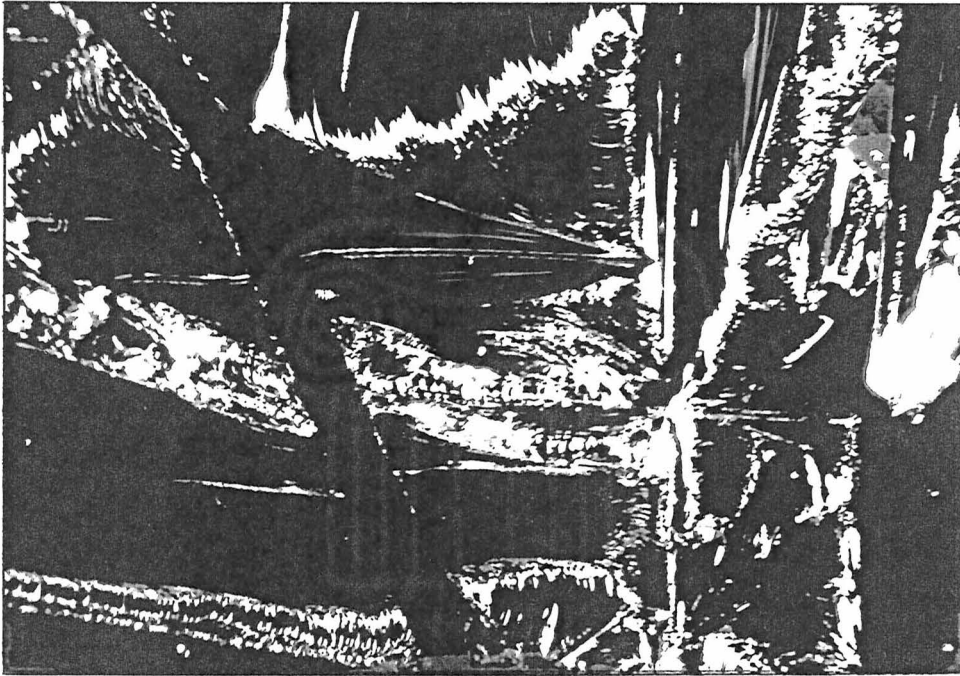


Figure 6.4(a)

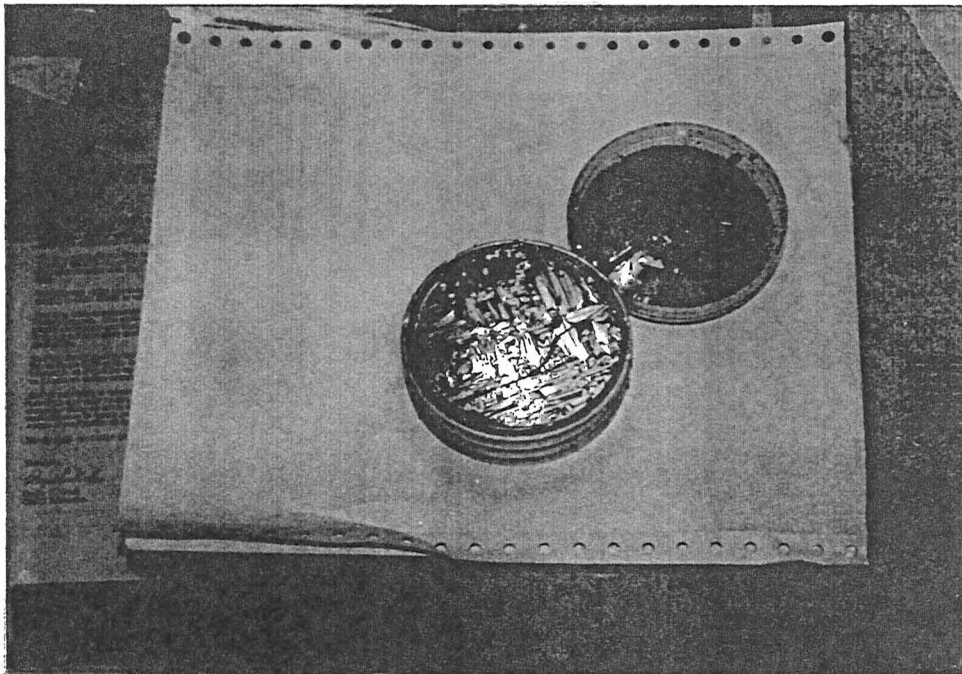


Figure 6.4(b)

Figure 6.4(a) Micrograph of the surface of silicon wafer with most of the thick boron film peeled off. Note the roughness of the surface because parts of the silicon on the surface are taken off with boron film. (b) Photograph of the whole wafer. Note the crack caused by the stress between boron film and silicon.

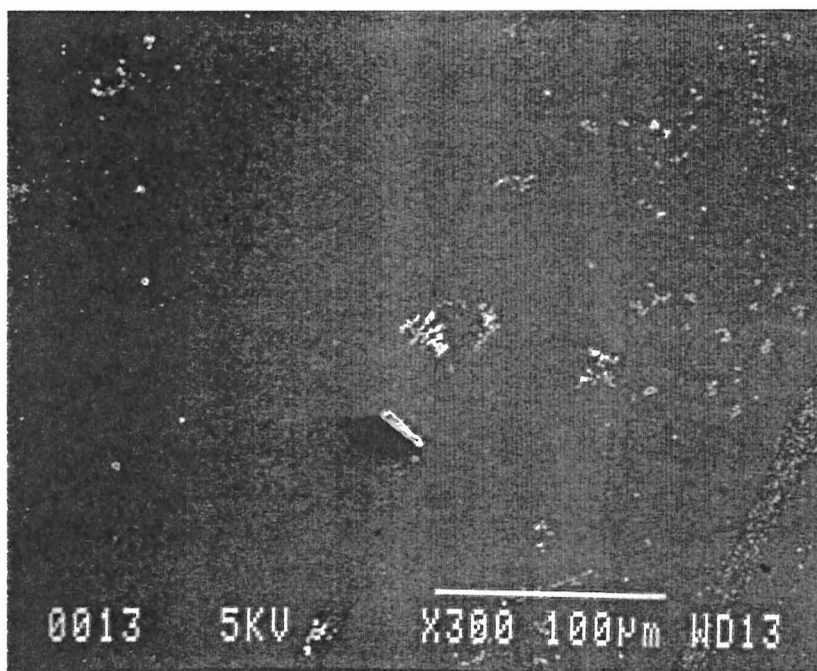


Fig.6.5 Scanning electron micrograph of the boron window.

VII. CHEMICAL ETCHING OF BORON FILM

7.1 Introduction

CVD amorphous boron, generally speaking, is quite chemically stable. Its stability suggests several questions. First, can it withstand the attack of a variety of acids and bases? If so it can be used as a hard, low Z coating for corrosion protection in special surroundings. Second, what kind of chemical solutions can etch boron films effectively so that they can be patterned successfully? And what are their etch rates? Knowing this is very important if we want to apply boron films widely in industry.

We have determined the etch rate of a-B:H in some media and have found some solutions which can be used as etchants for boron.

7.2 Procedures and Results

To find the etching rate of boron film we have to first find a good way to determine the thickness of boron film. Here the Perkin Elmer 320 was used to measure the exact position of the interference fringes of a boron film deposited on a silicon wafer. As we know, for the two adjacent maxima of the fringes the following simultaneous equations exist (see the previous chapter):

$$\begin{aligned}2nd\cos\alpha &= m_1\lambda_1 \\2nd\cos\alpha &= m_2\lambda_2,\end{aligned}\tag{7.1}$$

where m_1, m_2 are consecutive integers, $m_2 = m_1 - 1$.

Here we assume that optical index, n , does not vary with the wavelength. Indeed, for λ_1 close to λ_2 , n will not change much even for dispersive materials and the assumption that n is effectively constant is reasonable. We obtain the following relationship:

$$m_1 = \frac{\lambda_2}{\lambda_2 - \lambda_1} \quad (7.2)$$

Substituting (7.2) into any one of the simultaneous equations (7.1) we can find the optical thickness. Since we already know n for certain wavelengths in Chapter 4, we can determine the film's thickness, d .

If the etching rate were constant, then only the initial and final thicknesses and the etching time would need to be known to determine the etching rate. However, we can not conclude that the etching rate is constant. Measurements must be at many intermediate steps.

The method mentioned above has some limitations, i.e., prior to etching the thickness of the born film must be uniform and not excessive or else we could not clearly see the fringes when we measure the reflectance of the sample. Also if the etching rate is very high (micrometers/minute), the optical method is not a good method to measure the thickness of the film. Instead, for samples with high etch rates we can use a stylus method to measure the change in thickness.

The following is the procedure we used for the stylus method. We applied to the boron coated surface of the silicon wafer, several strips of Kapton tapes, each one partially overlapped by another. During etching we could periodically take

the sample briefly out of the etching bath, remove off one strip of Kapton tape so that another step would be exposed and return the sample to the solution. We then found the etching rate at several intermediate times by using the stylus method to measure the heights of the steps. This method does not limit the original thickness of the boron film so that we can utilize thick boron films on silicon wafers in the test. Since the scan range of the stylus instrument is more than 100 μm the slope of the step causing by the etching under the tape will not influence the measurement of its height.

Using the above routine we can find the thickness of the boron film after each etching so that the etching rate can be found. On the following page there is a table which indicates the etching rate against boron film for various etchants.

From that table we have found that the boron films are very stable in bases and concentrated nonoxidizing acids such as concentrated HF, HCL, H_3PO_4 , H_2SO_4 , and glacial acetic acid. The etch rate in oxidizing acids, such as concentrated nitric acid and aqua regia, is measurable—about 3 $\mu\text{m}/\text{day}$. The etch rate in oxidizing bases such as permanganate and ferricyanide is high, approaching 1 $\mu\text{m}/\text{min}$. (the contents of the solutions are listed in the following table).

It is noted that in a very few case the apparent thickness of the film increases. The negative sign before the etch rate indicates that the boron films apparently have become thicker after etching. The reason for this is unknown. Perhaps a surface chemical reaction occurred which caused the film to swell by

incorporating atoms from etchant solutions.

THE TABLE OF ETCHING RATE OF BORON FILMS

Etching Reagents*	pH	Etch Rates nm/min at	
		Room Temperature	
		Beryllium	CVD a-B:H
HF	0.8	fast	neg.
H ₂ SO ₄	-1.3	6060	-4.0×10^{-4}
HNO ₃	-1.17	10.7	1.09
Acetic Acid	1.8	45	-0.079
H ₃ PO ₄	-1.17	1160	0.146
Aqua Regia+	-1.0		0.14 ± 0.02
NH ₄ OH+H ₂ O ₂	11.4	neg.	neg.
NaOH Solution++	13.7		neg.
Ferricyanide**	13.7	1.5	165
Permanganate#	13.7		900

* All are concentrated unless otherwise indicated;

** Solution is 0.6M in K₃Fe(CN)₆, 0.5M in NaOH, 0.02M in Oxalation;

+ Solution is 1M in HNO₃, 3M in HCl, 1M in H₂O;

++ Solution is 0.5M in NaOH, 0.6M in H₂O₂;

Solution is less than 0.6M in KMNO₄, 0.5M in KOH.

VIII. The APPLICATION OF AMORPHOUS BORON FILMS IN X-RAY IMAGING

Since boron has a low absorption coefficient to x-rays, it can be useful for x-ray imaging. The main applications I have been studying are in the following two fields: one is a boron coating on beryllium windows which can protect them from corrosion and chemical attack; the other is self-supporting boron window fabrication.

8.1 Boron Coating on Beryllium as a Corrosion Barrier Layer

X-ray tubes produce x rays by the impact of energetic electrons on a target. The x rays produced are radiated in all directions and some of them reach the region where they are used after passing through a window. The window separates the working area from the x-ray production environment where a high vacuum is needed and which must be contamination free. The window must be transparent enough to pass as many x rays as possible. It also must be reliable enough to maintain the integrity of the x-ray tube for many years. There are no materials which are entirely transparent over all of the x-ray band. It has been found that beryllium is the only material suitable for x-ray tubes and in the thickness required it has substantial absorption particularly for soft x-rays. On the other hand, beryllium is strong and tough enough to be useful for most purposes and has been used with few changes for more than half a century. There is a trend to thinner windows which has made them more subject to

failure. The current state of the art is 5 mil (127 microns) thickness.

We learned that these and thinner windows are subject to failure as leaks develop. In normal noncorrosive environments leaking begins after several years. This leaking was due to galvanic corrosion occasioned by the contact of dissimilar metals and an electrolyte. Beryllium is chemically active and more strongly electropositive than the stainless steel walls of the vessel to which it is attached. There is no way to avoid the contact of dissimilar metals and since beryllium is more chemically active it will always be the active member of the couple attacked. That there may be an electrolyte present is not clear, however, the electrolyte can be any salt bearing region. It is not always a liquid, and sometimes it appears to follow the pattern of a finger print suggesting that this is the source of the salt/electrolyte.

The only approach which has occurred to researchers is to overcoat beryllium with one or more films which have very low absorption, are inert, tough and chemically resistant and will deny the access of electrolytes and salts in any form to the beryllium window. It is highly desirable to use low Z materials for protecting beryllium but there are few viable choices. Lithium is chemically active, the rest of the elements of that row in the periodic table are gases except for carbon and boron.

We discovered that amorphous boron films can stick well to the surface of the beryllium and can be deposited without stress related failure to thicknesses

of many microns if required. The boron coated beryllium windows are chemically stable (see Chapter VII). They are also hard and can resist the effect of abrasion (see Chapter V).

We successfully coated 1 μm of boron on a beryllium window of 1 mil in thickness. It is surprisingly stable in both a radiation and a chemically aggressive environment. It is found that HF acid, which can easily etch beryllium, cannot attack beryllium with a boron coating. We put the sample window in front of the x-ray source, kept the source working for thousands of hours and no damage was found. The film was also found to be chemically and abrasion resistant with unexpected (2000 to 3000) Vickers hardness. Fig. 8.1 shows the coated beryllium window with a boron film.

8.2 The Fabrication of Boron Windows

Though beryllium foils are made by crossrolling a sheet of a compressed beryllium powder, it cannot be very thin. About 1 mil in thickness is the minimum size. Pinhole free can be maintained. Also, it is toxic and chemically active. CVD boron films can be very thin. The absorption coefficient for boron is larger than that of beryllium, but the attenuation of x-ray through boron windows can be smaller than that through beryllium windows if the boron windows are thin enough. We successfully fabricated a boron window by depositing the boron film and then etching the silicon off according to a certain pattern. Appendix 6 indicates all the whole processing steps. Fig. 8.2 is a picture of a boron window

taken by scanning electron microscope.

Boron windows of 1 μm in thickness were fabricated successfully without pinholes. They are unfortunately too weak to withstand one atmosphere differential between both sides for the windows without a rib structure. However, if we improve the window structure by adding ribs, perhaps they can adequately support the required differential. Since the boron films have many properties which are especially useful for x-ray applications I think that this technique will contribute greatly to x-ray devices; not only for the x-ray windows, but also for multilayer, bending, x-ray beam splitters, etc.

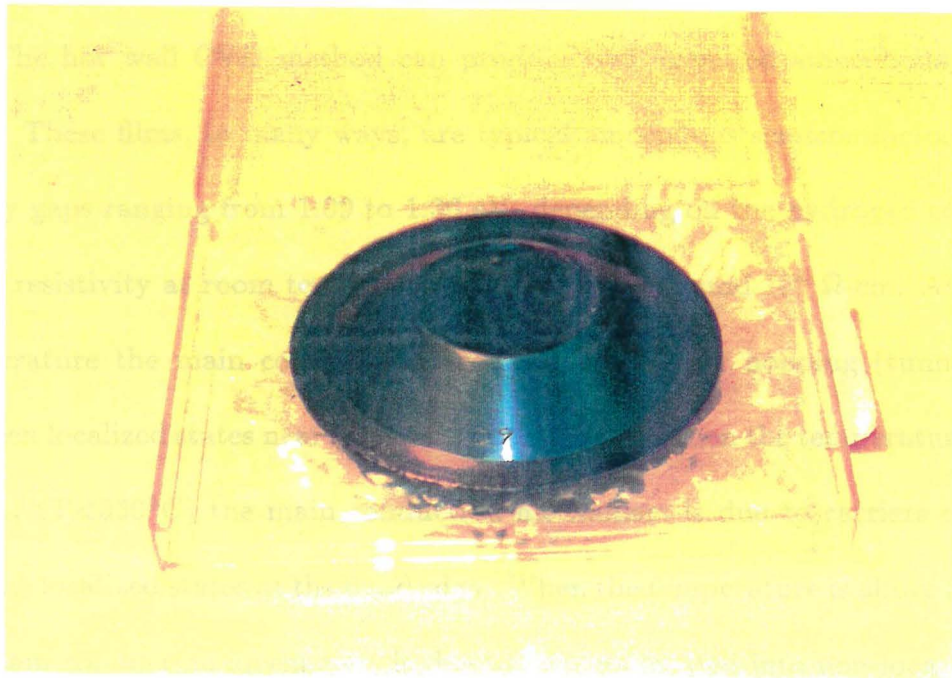


Fig. 8.1 Photograph of the beryllium window coated with boron thin film.

IX. SUMMARY

9.1 Conclusion

The hot wall CVD method can produce hydrogenated amorphous boron films. These films, in many ways, are typical amorphous semiconductors with energy gaps ranging from 1.09 to 1.36 eV, depending on the hydrogen content. Their resistivity at room temperature is as high as around $10^4 \Omega\text{-cm}$. At room temperature the main conduction mechanism is carrier hopping (tunnelling) between localized states near the Fermi energy level. When the temperature rises ($T_{room} < T < 350^\circ\text{C}$) the main conduction mechanism is due to carriers excited into the localized states at the band edge. When the temperature is above 350°C , the main conduction mechanism is due to carriers excited into non-localized or extended states. The Young's modulus of the boron film is $3.05 \times 10^{13} \text{ dyne/cm}^2$. The intrinsic stress of boron films on silicon wafers with (110) orientation is $9.03 \times 10^9 \text{ dyne/cm}^2$. The hardness is around 2500 Vickers.

Boron thin films are quite stable chemically and nontoxic. They are very stable in nonoxidizing bases and concentrated nonoxidizing acids such as concentrated HF, HCL, H_3PO_4 , H_2SO_4 , and glacial acetic acid. The etch rate in oxidizing acids, such as concentrated nitric acid and aqua regia, is $3 \mu\text{m/day}$. The etch rate in oxidizing bases such as permanganate and ferricyanide is high, approaching $1 \mu\text{m/min}$. With those etchants we can produce various patterns in boron films.

Since boron is a low Z element, it is very useful for making x-ray imaging devices. It can be a hard passive layer for beryllium x-ray windows. There is evidence that boron thin films may have a bright future in making x-ray imaging devices.

9.2 Future Work

I think that the following topics are worth studying further:

(1) studying how the stress of the boron films vary with the condition of production. Chapter 6 mentioned that the stress of the boron films will change with the conditions of production. It would be very useful to the bending work for x-ray imaging.

(2) studying the interface between beryllium and CVD boron films deposited at high temperature. Studying how they diffuse and what optical effect the sample will have, such as the reflectance and transparenence. This would be helpful to the baffle work for x-ray imaging;

(3) studying further the deposition conditions and x-ray optical properties of boron films. For example, we need to find what is the proper deposition conditions to improve the surface smoothness of boron films; we also need to find the soft x-ray properties for self-supporting boron films. It is a challenging task to find more applications of boron film in x-ray imaging.

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APPENDIX 1

Silicon Wafer Cleaning Procedure

1. soak in hot 50 : 50 decontam solution for longer period than 10 minutes.
 - a. prepare solution with 400ml decontam and 400ml distilled water;
 - b. heat to boiling point.
2. rinse in running distilled water for longer period than 5 minutes.

empty rinse container completely at least once during rinse.
3. soak in 5% HF solution for 10 minutes.
 - a. prepare solution with 80ml of 49% HF and 800ml of distilled H_2O ;
 - b. do not soak for long periods of time or a white film will develop.
4. repeat rinse.(see step 2)
5. blow to dry the sample with N_2 or methanol.

APPENDIX 2

Infrared absorption bands at room temperature of amorphous boron films (pure and doped with hydrogen and/or carbon, pure β -rhombohedral boron, and boron carbide ($B_{12}O_3$))

center of band (cm^{-1})	amorphous boron films ^{a)}				bulk amorphous boron [3, 9]	polycryst β -rhombo. boron [7, 8]	boron carbide [10, 11, 21]	comments
	pure	H ₂ -doped	O-doped	O ₂ H ₂ -doped				
2500	n. o. ^{a)}	sharp band	n. o.	sharp band	B-H stretch unk. ^{a)} impurity	n. o.	n. o.	hydrogen
2000	n. o.	n. o.	n. o.	n. o.		n. o.	n. o.	
1550	n. o.	n. o.	n. o.	n. o.	n. o.	n. o.	med., sharp	B ₁₂ O ₃ lattice B-O vibration [2]
1350	very wk. ^{b)}	very wk.	very wk.	very wk.	n. o.	very wk.	n. o.	
1250	n. o.	n. o.	n. o.	n. o.	n. o.	med.	n. o.	
1000	broad, wk.	broad, wk.	broad, strong	broad, strong	broad, strong	strong (several) 900 to 1100 cm^{-1}	strong	lattice and carbon
800	broad, wk.	broad, wk.	broad, wk.	broad, wk.	broad, med. ^{d)}	med. bands	strong in B-B ₁₂ O ₃ mix wk. in pure B ₁₂ O ₃	lattice

^{a)} Results in the first four columns are from this work.

^{a)} Not observed. ^{b)} Weak. ^{c)} unknown ^{d)} medium strength

APPENDIX 3

```

C *****
C PROGRAM DESCRIPTION
C This program can find the optical index n and k of the sample from its
C reflectance and transmittance for each wavelength according to the
C schematic diagram shown in Chpter 4.
C
C VARIABLE LIST
C n(I)          optical index of the film;
C k(I)          imaginary part of the optical index of the film;
C d            thickness of the film;
C s(I)          optical index of the micro slide;
C refle(I)      reflectance of the sample;
C t(I)          transmittance of the sample;
C para         reflectance of the mirror at certain angle;
C lamda(I)      wavelength (in nm).
C
C PROGRAM OUTPUT
C lamda(I), n(I), k(I).
C *****
      double precision refle(10),k(10),d,n(10),t(10),s(10)
      double precision para
      integer lamda(10),tem,m(10),num
      write(6,*)'please input the reflectance of mirror'
      read(5,*)para
      write(6,*)'please input the thickness'
      read(5,*)d
      write(6,*)'Please input the number of data'
      read(5,*)num
      do 10 j=1,num
      write(6,*) 'Please input the wavelenghtes of reflection
& from 500nm to'
      write(6,*)'820nm . The wavelength (in nm)='
      read(5,*) lamda(j)
      write(6,*)'Its value of reflection='
      read(5,*)refle(j)
      write(6,*)'its transmission value='
      read(5,*)t(j)
      write(6,*)'its substrate index='
      read(5,*)s(j)
      type *, 'please input initial k.'
      read(5,*)k(j)
      rfm1=refle(j)/para**2
      call determin(t(j),rfm1,n(j),k(j),d,s(j),lamda(j))
10      continue
      do 300 j=1,num
      write(6,30)lamda(j),n(j),k(j)
300      continue
30      format(1x,I6,7x,F9.3,4x,F9.3)
      stop
      end
C *****

```

```

C   Evaluate n and k of the sample at the given wavelength. This
C   subroutine needs to input the range of n at the given wavelength.
C   *****
      subroutine determin(t1,r1,n1,k1,d,s1,y1)
      double precision t1,r1,n1,k1,d,a1,a2,s1,high,low
      integer y1
      type *,'input low and high n'
      read(5,*)low,high
      call findn(r1,k1,d,y1,s1,n1,low,high)
      a1=k1
      a2=n1
      k1=findk(t1,n1,d,s1,y1)
      do while((abs(a1-k1).ge.0.001) .or.(abs(a2-n1) .ge.0.01))
        a2=n1
        call findn(r1,k1,d,y1,s1,n1,low,high)
        a1=k1
        k1=findk(t1,n1,d,s1,y1)
      enddo
      return
      end

C   *****
C   This function is to find k of the film at the given wavelength. Here
C   equation (4.12) is used.
C   *****
      double precision function findk(t,n,d,s,y)
      double precision t,n,d,s,temp
      integer y
      temp=(n+1)**3*(n+s**2)*t
      temp=temp/(16*n**2*s)
      temp=LOG(temp)
      temp=-y*temp/(4*3.1415926D0*d)
      findk=temp
      return
      end

C   *****
C   This subroutine is to find n of the film according to the reflectance
C   at a given wavelength. If the initial value of n is proper, "ok" will
C   be shown on the screen.
C   *****
      subroutine findn(x,y,d,lamda,s,n,a,b)
      double precision a,b,c,x,y,dd1,dd2,lamda,s,n
*      a=2.8D0
*      b=2.85D0
      c=a+(b-a)/2
      call result(x,y,c,d,lamda,s,dd1)
      do while (dabs(dd1).ge. 0.01)
        call result(x,y,a,d,lamda,s,dd2)
        if(dd1*dd2.gt. 0.0) then
          a=c
          c=a+(b-a)/2
        else
          b=c

```

```

        c=a+(b-a)/2
    endif
    call result(x,y,c,d,lamda,s,dd1)
end do
n=c
write(6,*)'ok'
return
end

```

```

C *****
C   This subroutine is to find the difference between the given
C   reflectance and the calculated reflectance from the given n and k.
C   Equation (4.13) is used here.
C *****

```

```

    subroutine result(x,y,c,d,lamda,s,dd)
    real x,y,c,p,q,d,s,dd,a
    complex r1s,r2s,rs3,rs,b,j
    integer lamda
    p=sqrt((c**2-y**2-0.25D0)**2+4*c**2*y**2)
    p=p+(c**2-y**2-0.25D0)
    p=sqrt(p/2)
    q=sqrt((c**2-y**2-0.25D0)**2+4*c**2*y**2)
    q=q-c**2+y**2+0.25D0
    q=sqrt(q/2)
    j=cmplx(0.D0,1.D0)
    r1s=(1.732D0/2-p-j*q)/(1.732D0/2+p+j*q)
    r2s=(p+j*q-sqrt(s**2-0.25D0))/(p+j*q+sqrt(s**2-0.25D0))
    rs3=(sqrt(s**2-0.25)-0.866025)/(sqrt(s**2-0.25)+0.866025)
    b=4*3.1415926D0*d/lamda*(p+j*q)
    a=4*3.1415926*d*sqrt(s**2-0.25)/lamda
    rs=r1s+r2s*exp(j*b)
    rs=rs/(1+r1s*r2s*exp(j*b))
    r3s=(1-r1s**2)*(1-r2s**2)*r3s*exp(j*a+j*b)/(1-r1s*r2s*exp(j*b))
    rs=rs+r3s
    dd=rs*conjg(rs)-x
    return
end

```


APPENDIX 4

$\lambda(nm)$	n	k
1779	2.84	0.016
1516	2.91	0.026
1167	2.98	0.054
864	3.19	0.103
743	3.33	0.157
685	3.37	0.188
637	3.44	0.220
575	3.45	0.274
550	3.46	0.300
530	3.48	0.320
510	3.49	0.347
490	3.50	0.374
470	3.51	0.403

The above table indicates the refractive index of n and k for the thin film deposited at 3 inches from the entrance of the hot zone.

$\lambda(nm)$	n	k
1466	3.06	0.044
850	3.23	0.137
810	3.27	0.148
707	3.37	0.206
610	3.53	0.271
570	3.53	0.311
520	3.56	0.366
490	3.59	0.407
470	3.61	0.437
450	3.63	0.463

The above table indicates the refractive index of n and k for the thin film deposited at 4 inches from the entrance of the hot zone.

APPENDIX 5

The main procedures of fabricating boron windows are as follows:

1. clean the silicon wafers;
2. deposit a boron film on a silicon wafer;
3. etch the boron film on one side of silicon wafer;
4. using microlithography method make a pattern on that side of the silicon wafer;
5. etch the silicon off according to the pattern.

Characterization of Boron Films Prepared by Chemical Vapor
Deposition and their Applications in X-ray Imaging

Fang Yuan

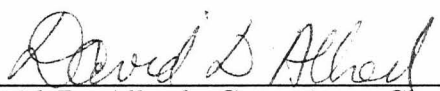
Department of Physics and Astronomy

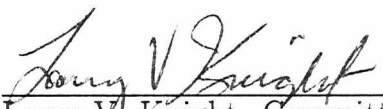
Ph.D. Degree, November, 1991

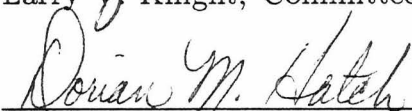
ABSTRACT

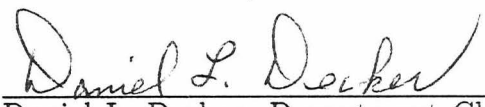
Boron, a low Z element, is useful for x-ray optics since it has a low atomic absorption coefficient. Boron films prepared by chemical vapor deposition were characterized optically, electronically and mechanically. Auger, infrared and hydrogen effusion analyses showed that the films are amorphous hydrogenated boron. The hydrogen content ranges from 8% to 71%. The measurements of the complex refractive index and the resistance vs. temperature determined that they are typical amorphous semiconductors with the energy gap ranging from 1.09 eV to 1.36 eV, decreasing with increasing hydrogen content and the Fermi energy level is pinned about midgap. The real refractive index at 490 nm increases from 3.25 to 3.59 with increasing hydrogen content. The Young's modulus and hardness were found to be 3.05×10^{13} dyne/cm² and around 2500 Vickers, respectively. A method of measuring optical index of boron films is proposed and described, as well as a model that determines their Young's modulus and predicts the bending of the boron/silicon structure. The chemical tests suggested that boron films are stable in nonoxidizing bases and concentrated acids. Some oxidizing bases such as a basic ferricyanide solution are good etchants for CVD boron films. Boron coating on beryllium windows as a corrosion barrier layer and self-supporting boron windows are set forth as potential products of x-ray imaging.

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