Analysis of the plastic substrates, the reflective layers, and the adhesives of today's archival-grade DVDs

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ABSTRACT

The plastic substrates, reflective layers, dyes, and adhesives of four archival-grade DVDs and one standard-grade recordable DVD were analyzed to determine their chemical compositions and/or physical dimensions. Chemical analyses by ATR-FTIR, ToF-SIMS, XPS and EDX/STEM show that all these DVDs use very similar polycarbonate plastic substrates and acrylate-based adhesives, but different reflective layers and dye write layers. In addition, physical measurements by AFM show differences in the DVD groove depth, width, and other dimensions. These chemical and physical analyses may help explain variations in DVD lifetimes and facilitate development of the next generation of archival-grade DVDs.

Keywords: DVDs, plastic substrates, reflective layers, adhesives, dyes, DVD groove dimensions, ATR-FTIR, ToF-SIMS, XPS, AFM, EDX/STEM.

1. INTRODUCTION

With the increasing need for long-term data storage, so-called archival-grade DVDs that could provide hundreds of years of data storage, as sometimes claimed, have appeared on the already confusing multi-format, multi-product DVD market. Compared to standard-grade DVDs, archival-grade DVDs appear to use more stable dyes to improve DVD lifetimes.[1-2] Some manufacturers also claim scratch-resistant coatings and/or gold reflective layers in their archival-grade DVDs for longer DVD lifetimes.[2-3] Recent longevity tests by Lunt and Linford showed large lifetime variations among different brands of commercial archival-grade DVDs, as well as standard-grade DVDs on the market.[4] Since DVDs' lifetimes are most likely determined by their chemical compositions, the large lifetime variations among the tested DVDs, therefore, suggests that those DVDs' chemical compositions are different. Like standard-grade DVDs, except for perhaps a more stable dye write layer, a typical archival-grade DVD will have plastic substrates, a metal reflective layer and a binding adhesive layer. Differences in chemical composition of any one or more of these DVD layers may influence the lifetime of DVDs.

Here, to understand the chemical compositions of DVDs and DVD lifetime determining factors, we analyzed chemical compositions of individual layers of four brands of archival-grade DVDs and one standard-grade DVD using chemical analysis methods. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was used to analyze the plastic substrates and the adhesives. X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were used to analyze the reflective layers. One reflective layer's cross-section sample was further analyzed with energy-dispersive X-ray spectroscopy (EDX) using a scanning transmission electron microscope (STEM) to determine the thickness and composition of the deposited gold layer. These chemical analyses show that these DVDs use very similar polycarbonate substrates and (most likely) acrylate-base adhesives, but different reflective layers and dye write layers. In addition, atomic force microscopy (AFM) was used to measure the physical dimensions of the grooves on the DVD plastic substrates. The AFM measurements also show that the DVD grooves had different physical dimensions. These analyses may reveal the factors that influence DVD lifetimes and thus help the development of future archival-grade DVDs.

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2. EXPERIMENTAL

Attenuated total internal reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed on a Nicolet 6700 FTIR spectrometer with a Smart Orbit diamond ATR accessory (Thermo Scientific, Waltham, Massachusetts). The ATR-FTIR measurements of the plastic substrates from four archival-grade DVDs, denoted A1, A2, A3, and A4, were taken on the outside of their L1 substrates, near the center hole, which was free of labels. The ATR-FTIR measurement of the plastic substrate from one standard-grade DVD, denoted S1, was taken on the outside of its L0 substrate, as the outside of its L1 substrate was almost fully covered by its disc label. The ATR-FTIR measurements of the adhesives from the four archival-grade DVDs and one standard-grade DVD were taken on the inside of the polycarbonate substrates near the center holes where the adhesives remained after disc splitting.

X-ray photoelectron spectroscopy (XPS) was performed on an SSX-100 spectrometer (Service Physics Inc., Bend, Oregon) that is equipped with an Al Kα X-ray source and a hemispherical detector. For the XPS analysis, the DVDs were split into L0 and L1 halves to expose their reflective layers. The exposed reflective layers may remain on either the L0 halves (reflective layer's back side is exposed, facing L1) or the L1 halves (reflective layer's front side is exposed, facing L0). After splitting, the front sides of the reflective layers were usually covered by a thin layer of dye that could be rinsed away using acetone prior to the analysis, and although the back sides of the reflective layers were sometimes contaminated by DVD-binding adhesives, they could generally be analyzed directly without cleaning.

ToF-SIMS analysis was performed on an ION-TOF ToF-SIMS IV system (ION-TOF GmbH, Münster, Germany) with a Ga ion source in bunched mode. Sample preparation for ToF-SIMS analysis is identical to that for XPS analysis. Positive ion spectra were acquired from the reflective and dye layers with a sampling size of 500 μm × 500 μm contained in 256 pixels × 256 pixels obtained by random rastering.

EDX analysis of a DVD reflective layer cross-section was performed on a Technai TF20 analytical TEM (FEI, Hillsboro, Oregon). Scanning transmission electron micrographs were obtained using a 200 kV electron beam. EDX line profiles were then extracted from the micrographs running perpendicular to the reflective layer. For this analysis, the exposed reflective layer was coated with a protective carbon film approximately 60 nm thick by thermal deposition, and then loaded into a Helios Nanolab 600 DualBeam (FEI) focused ion beam (FIB) system with a gallium ion source. A 1 micron pad of platinum was deposited in the FIB system for further protection. A final cross-sectional sample 16 μm long, 4.5 μm wide and 8 μm tall was milled out by FIB and welded onto a TEM grid. The region of interest from the sample was further thinned to less than 70 nm for the STEM analysis.

AFM measurements were performed on a Dimension V Atomic Force Microscope (Veeco, Plainview, NY). For AFM measurements, the areas of the L0 halves that had DVD grooves but no reflective layers remaining were cut out, rinsed with 2-propanol to remove dye residues, and then dried with a jet of N_2.

3. RESULTS AND DISCUSSION

Since all DVDs use plastic substrates as the base physical support materials, the physical and chemical properties of the plastic substrates are essential to DVDs. The ATR-FTIR spectra of the A1-4 and S1 plastic substrates were compared to that of a known sample of bisphenol A polycarbonate (referred to herein as "polycarbonate") and are shown in Figure 1. It is clear that the ATR-FTIR spectra of all the plastic substrates are essentially identical, and that they are the same as that of the known sample of polycarbonate. In other words, all the DVDs that were investigated here, both the archival-grade and standard-grade, appear to use very similar if not identical polycarbonate materials as their plastic substrates.

The DVDs' L0 and L1 halves are glued together with adhesives, and the properties of a DVD adhesive are believed to affect the DVD's lifetime. We analyzed the adhesives of the A1-4 and S1 DVDs using ATR-FTIR. Figure 2 shows the ATR-FTIR spectra of the A1-4 and S1 adhesives left behind on their plastic substrates, as well as the polycarbonate control. The fact that the spectra are so similar, even throughout the fingerprint region of the spectra, suggests that all the adhesives used in the A1-4 and S1 DVDs are identical. On the other hand, this result also indicates that, for the A1-4 and S1 DVDs, their adhesives are not the determining factor for their lifetimes. In addition, compared to the polycarbonate control's FTIR spectrum, all the adhesives' carbonyl peaks shift to lower wavenumbers (at ~ 1700 cm^{-1}) compared to the

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polycarbonate's C=O peak (at ~ 1750 cm^{-1}), which was not in the adhesives' spectra. Also, the peaks in the C-O stretching region of the adhesives' spectra show different shapes from the polycarbonate's C-O peaks. These observations suggest that the ATR-FTIR analyses of the adhesives were not influenced by their polycarbonate substrates. In addition, the C=O, C=C, and C-O peaks in the adhesives' FTIR spectra are consistent with them being UV-curable, acrylate-based adhesives.[5-7]

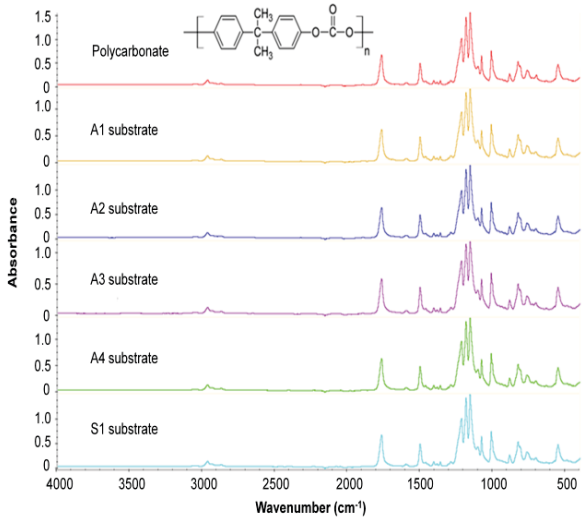


Fig. 1. ATR-FTIR spectra of the A1-4 and S1 substrates.

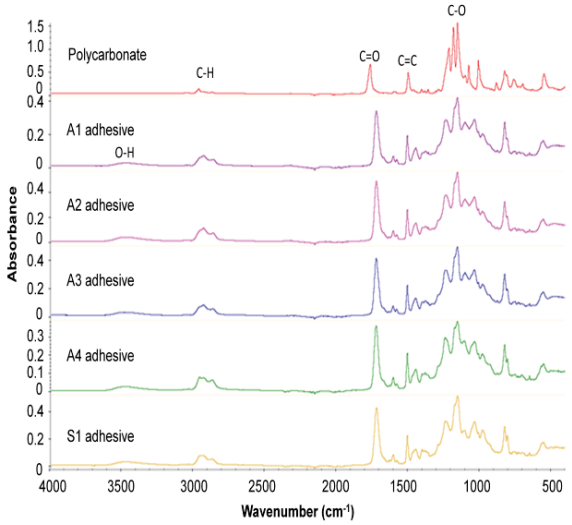


Fig. 2. ATR-FTIR spectra of the A1-4 and S1 adhesives.

Pure metals or metal alloys that have sufficient reflectivity to the laser writing/reading beams are used in DVDs as reflective materials, and DVD reflective layers usually show the color of the base metal or alloy (at least after discs are split apart). These reflective layers need to be chemically stable to maintain their required reflectivities. Figure 3 shows the XPS analysis of the reflective layers from the A1 and A2 DVDs. The survey spectra of both the front (facing L0) and back (facing L1) sides of the A1 and A2 reflective layers show the Au 4f, Au 4d, Au 4p, *etc*. peaks, all from gold, which appears to be the only metal present. Their front sides also show a few additional peaks from nonmetallic elements, including fluorine, carbon, and oxygen, while their back sides are generally much cleaner with only trivial amounts of carbon and oxygen. This XPS analysis indicates that both the A1 and A2 DVDs use only gold as their reflective layers. The gold color of the A1 and A2 reflective layers supports these XPS results. The nonmetallic elements observed in the spectra presumably come from dye residues (front sides), adhesives (back sides), and/or surface contamination.

Figure 4 shows the XPS survey spectra of the reflective layer of the A3 DVD. The survey spectrum of its front side (facing L0) indicates that, besides peaks from the nonmetallic elements carbon, oxygen and fluorine, as were also seen in the survey spectra of the A1 and A2 front sides, the only metal peaks present are Ag 3d and Ag 3p from silver (the top spectrum in Figure 4). However, the survey spectrum of its back side (facing L1), has peaks from both silver and gold: Ag 3d, Ag 3p, Au 4f, Au 4d, and Au 4p (see the middle spectrum in Figure 4). The XPS analysis of the A3 reflective layer's front side suggests that silver is used as the reflective layer in A3. The XPS analysis of its back side suggests that either a silver/gold alloy or a very thin gold layer is deposited on the back of the silver layer, as the XPS sampling depth is *ca.* 10 nm. This top metal film extends somewhat beyond the silver reflective layer, leaving a golden ring around the center hole of the disc. An XPS analysis of this golden ring, which was left on the L0 half (facing L1) after the disc was split, shows it to be pure gold (see the Au 4f, Au 4d, Au 4p, and Au 4s peaks in the bottom spectrum in Figure 4). This additional XPS analysis on the gold ring suggests that a very thin gold layer (thickness < 10 nm), rather than a silver/gold alloy, is used to cover the back side of the A3 DVD's silver reflective layer. XPS analyses of the reflective layer of A4 (not shown) resulted in the very same XPS spectra as that of the A3 DVD. Therefore, the XPS analyses of the A3 and A4 DVDs suggest that these products use silver as their reflective layers with thin gold layers behind them that may protect the silver reflective layers from oxidation. The colors of the front (silver) and the back sides (light gold) of the A3 and A4 reflective layers observed after splitting the discs also support these conclusions.

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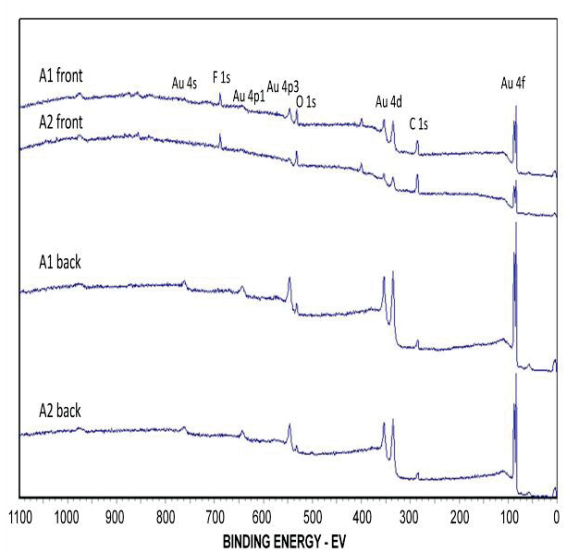


Fig. 3. XPS survey spectra of the A1 and A2 reflective layers.

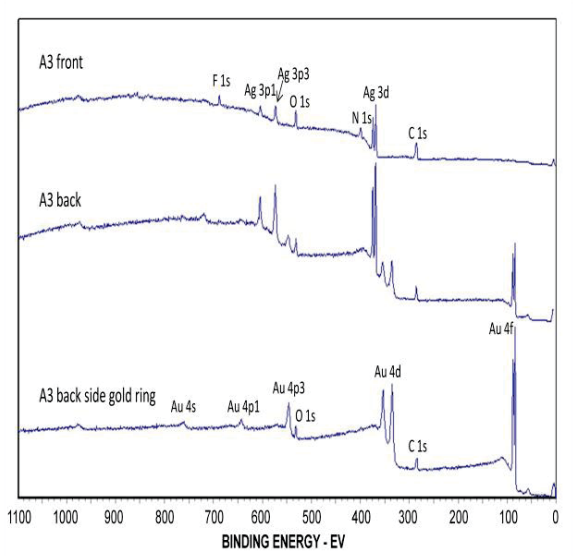


Fig. 4. XPS survey spectra of the A3 reflective layer.

Figure 5 shows the XPS survey spectra of the front and back sides of the S1 DVD's reflective layer. Silver and copper peaks (Ag 3d, Ag 3p, and Cu 2p) were seen in both spectra. These XPS spectra suggest that the S1 DVD uses a silver/copper alloy as the reflective layer, where its front and back sides are the same to within experimental error: the calculated alloy compositions (atom percentages) of the reflective layer from the corresponding XPS analyses were: 82% Ag + 18% Cu for the front side of S1, and 83% Ag + 17% Cu for the back side of S1. These results are supported by the S1 reflective layer's silver color on both its front and back sides.

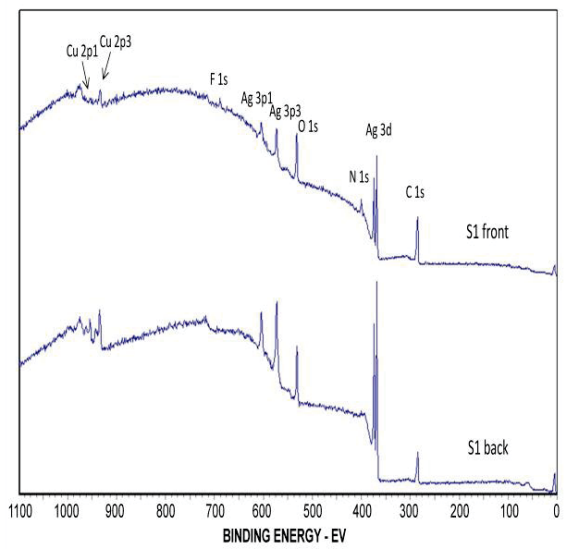


Fig. 5. XPS survey spectra of the S1 reflective layer.

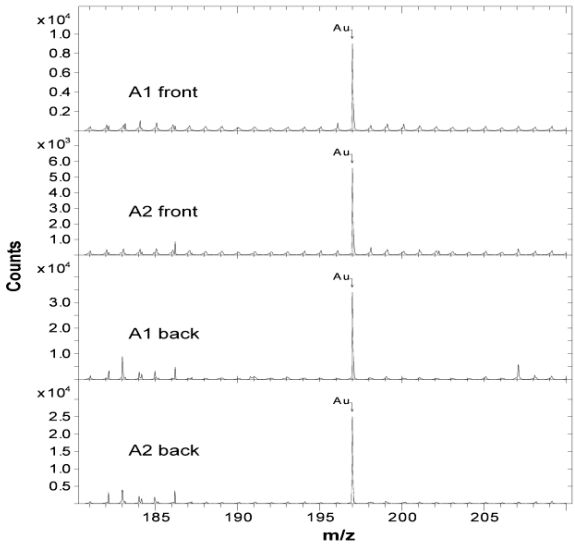


Fig. 6. ToF-SIMS spectra of the A1 and A2 reflective layers.

For further clarification of the identities of the metals used in the reflective layers of these archival-grade and standard-grade DVDs, the A1-4 and S1 reflective layers were analyzed by ToF-SIMS. Compared to XPS, ToF-SIMS is arguably a more sensitive and powerful technique in identification of metal elements, especially at the trace level. Figure 6 shows

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the ToF-SIMS spectra of the A1 and A2 reflective layers from m/z 180 to m/z 210. A strong gold peak, m/z 197, appears in the ToF-SIMS spectra of both the front and back sides of the A1 and A2 reflective layers. Trivial peaks corresponding to copper and/or silver were also found in the ToF-SIMS spectra of both the front and back sides of the A1 and A2 reflective layers (not shown). Non-trivial amounts of nickel and/or zinc, however, were found on the front sides of the A1 and A2 reflective layers (not shown), and no other common reflective metals' signals were observed. These ToF-SIMS and XPS analyses indicate that the A1 and A2 DVDs use only gold as their reflective layers, and that the trace amounts of copper and/or silver are likely from impurities in the gold films. That is, these results are consistent not only with the gold colors of both the front and back sides of the A1 and A2 reflective layers, but also with our previous XPS analysis that showed gold as the only metal present. The small nickel and/or zinc signals that are present in the ToF-SIMS spectra of the A1 and A2 reflective layers' front sides will be discussed below.

Figure 7 shows the ToF-SIMS spectra of the A3 and A4 DVDs' reflective layers. Strong silver peaks, ^{107}Ag at m/z 107 and ^{109}Ag at m/z 109, appear in both their front and back sides' spectra. In addition, small gold peaks at m/z 197 appear in their back sides' spectra, but do not appear in their front sides' spectra. Trace amounts of copper, likely from impurities, were also observed in the A3 reflective layer (front and back) by ToF-SIMS, and non-trivial nickel signals were found on both the A3 and A4 reflective layers' front sides by ToF-SIMS (not shown) – a possible source of these nickel signals will be described below. In the bottom of Figure 7 are the ToF-SIMS spectra of the gold rings that extend from the back sides of the A3 and A4 reflective layers towards their center holes. These gold ring spectra have a strong gold peak at m/z 197 compared to trivial silver peaks at m/z 107 and m/z 109, which indicates that these gold rings are essentially pure gold, as was previously observed in the XPS analysis.

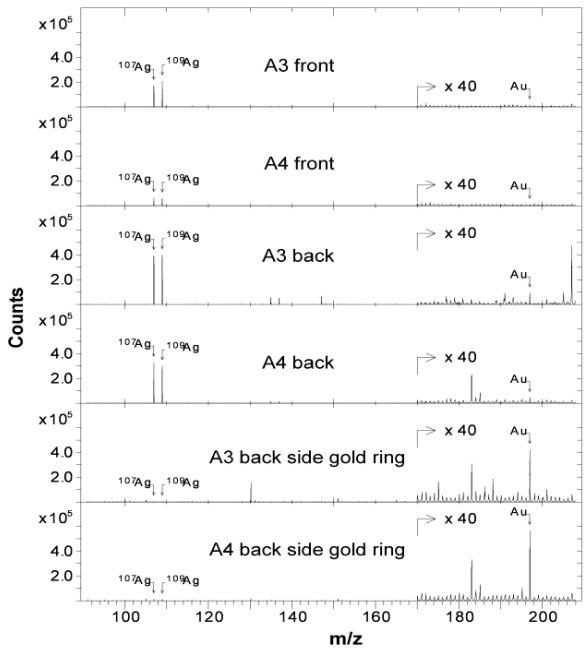


Fig. 7. ToF-SIMS spectra of the A3 and A4 reflective layers.

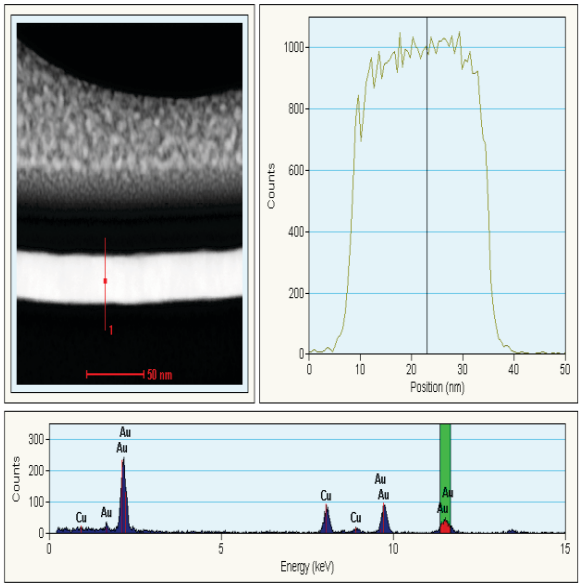


Fig. 8. STEM image (upper left), depth profile (upper right), and EDX spectrum (bottom) of the cross-section of the A4 reflective layer backside gold ring.

These ToF-SIMS spectra suggest that there is a silver layer on the front sides of the A3 and A4 reflective layers and a thin gold layer or a gold/silver alloy on their back sides, where the gold or Au/Ag layer may have been deposited to protect the silver reflective layer from oxidation. For further clarification, a cross-sectional sample milled from the A4 reflective layer backside gold ring underwent a STEM/EDX analysis. Figure 8 shows the resulting cross-sectional scanning electron micrograph, including an EDX line scan profile, across the gold layer extracted from the micrograph, and its corresponding EDX spectrum. The gold layer was approximately 30 nm thick, and its EDX spectrum shows the layer to be pure gold throughout. The copper peaks observed in the EDX spectrum are attributed to the copper grid used for sample mounting. Sputtering would be the logical way to deposit metal films on a DVD. Since sputtering is

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fundamentally a high energy process, these results raise the possibility of a significant amount of mixing between an initial silver reflective layer and a thin gold layer deposited over it during sputtering. This hypothesis is consistent with the A3 and A4 reflective layers' silver color on their front sides and lightgold color on their back sides, and is also supported by the XPS and ToF-SIMS analyses of the A3 and A4 reflective layers that showed strong silver signals on their front sides and gold and silver on their back sides. The fact that there appears to be considerably less Au than Ag in the ToF-SIMS spectra of the back sides of the reflective layers is consistent with gold's lower ion yield in ToF-SIMS.[8]

ToF-SIMS spectra of the S1 DVD reflective layer, which has a silver color on both of its sides, are shown in Figure 9. It can be seen that its front and back sides' ToF-SIMS spectra are very similar to each other, both showing strong silver peaks, ^{107}Ag at m/z 107 and ^{109}Ag at m/z 109, and reasonably strong copper peaks, ^{63}Cu at m/z 63 and ^{65}Cu at m/z 65. These ToF-SIMS data suggest that the S1 DVD uses an alloy of silver and copper as its reflective layer, which supports the previous XPS analysis.

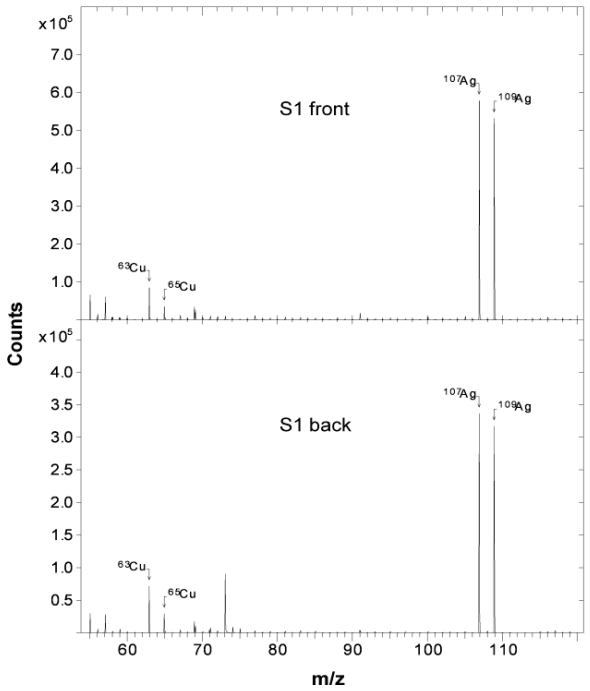


Fig. 9. ToF-SIMS spectra of the S1 reflective layer.

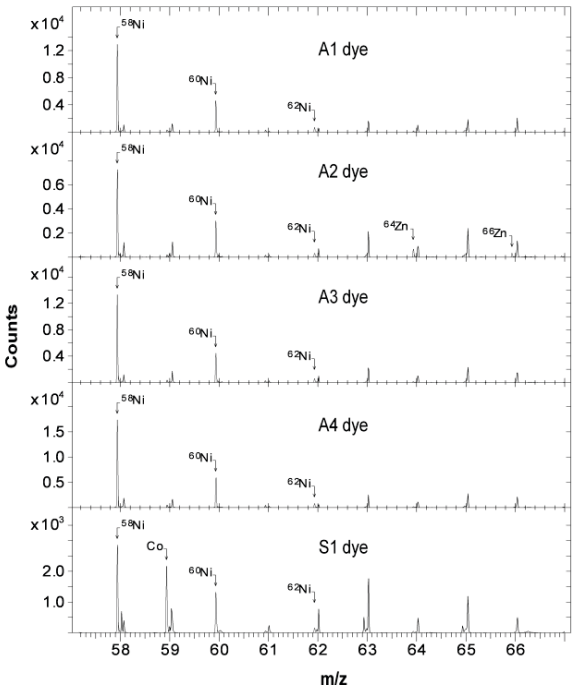


Fig. 10. ToF-SIMS spectra of the dyes from the DVDs that were analyzed.

Non-trivial nickel and cobalt peaks were also observed in the S1 reflective layer's front side ToF-SIMS spectrum (not shown). Indeed, the nickel peaks were observed in all of the reflective layers' front side ToF-SIMS spectra. These nickel peaks, the zinc peaks observed from the front side of the A2 reflective layer, and the cobalt peak observed from the front side of the S1 reflective layer are presumably from DVD dye residues, as all reflective layers' front sides are in contact with their dye layers. Accordingly, ToF-SIMS analyses of the A1-4 and S1 DVD dyes were then conducted (Figure 10). As expected, the nickel peaks were observed in all the dyes' ToF-SIMS spectra, while the zinc and cobalt peaks were observed in the A2 dye and S1 dye, respectively. It thus appears that the source of these metal signals is the dyes and not the reflectively layers. In particular, these metal signals may have originated from metal phthalocyanine or metal azo dyes.[9-12]

DVD grooves are physical features created on DVD L0 plastic substrates to guide laser beams along write/read digital data pits/marks within the DVD grooves. Thus, a DVD groove's design (shape, physical dimensions) is critical for the DVD, and it may also affect the DVD lifetime. Figures 11 and 12 show the A1 DVD grooves' 2- and 3-dimensional AFM images, respectively. Both the 2- and 3-dimensional AFM images show that the A1 DVD grooves are quite

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uniform and straight within the 4-5 µm by 4-5 µm sampling areas. Figure 13 shows an AFM profile that was drawn on the A1 AFM image across the grooves. The groove physical dimensions (depth, width, groove-to-groove distance, and pitch, see Figure 13) can then be extracted from the profile.

For comparison, average groove physical dimensions of all of the A1-4 and S1 DVDs were obtained by AFM and are listed in Table 1. We can see that the physical groove dimensions are all different, although, the physical dimensions of the A3 and A4 DVD grooves are quite close to one another.

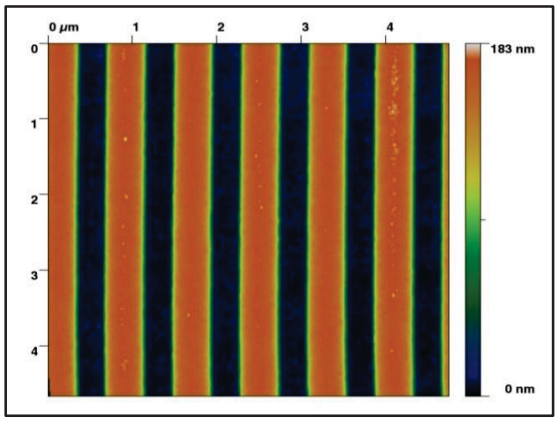


Fig. 11. 2-Dimensional AFM image of the A1 DVD grooves.

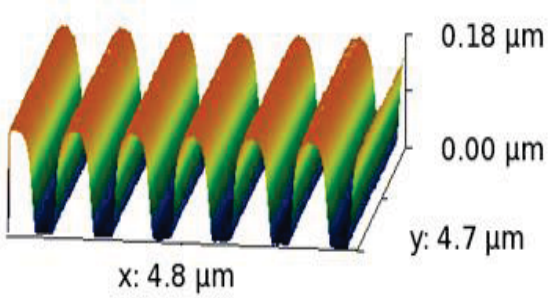


Fig. 12. 3-Dimensional AFM image of the A1 DVD grooves. (Same data as in Fig. 11.)

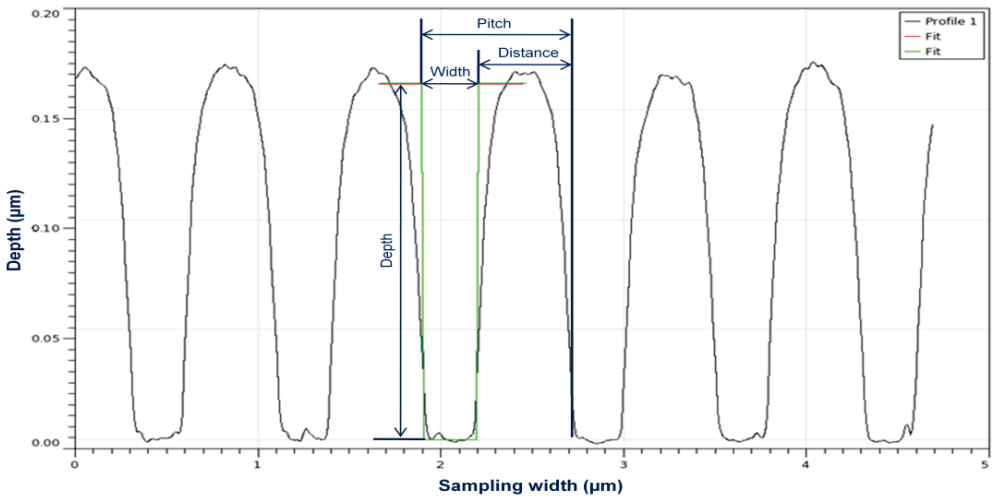


Fig. 13. Profile of the A1 DVD grooves.

Table 1. Average groove physical dimensions of the A1-4 and S1 DVDs by AFM (over multiple adjacent grooves).

	A1	A2	A3	A4	S1
Groove depth (nm)	164 ± 1	177 ± 2	176 ± 1	177 ± 1	150 ± 2
Groove width (nm)	320 ± 3	220 ± 5	293 ± 8	265 ± 9	202 ± 7
Groove-to-groove distance (nm)	472 ± 5	574 ± 6	489 ± 7	484 ± 13	519 ± 8
Pitch (nm)	792 ± 4	794 ± 4	782 ± 4	749 ± 5	721 ± 11

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4. CONCLUSIONS

ATR-FTIR, XPS, ToF-SIMS, STEM/EDX, and AFM analyses on the plastic substrates, adhesives and reflective layers of four archival-grade DVDs and one standard-grade DVD show that all of these DVDs use bisphenol A polycarbonates as their plastic substrates and very similar acrylate-based adhesives; the A1 and A2 DVDs use gold as their reflective layers, the A3 and A4 DVDs use silver that is protected with gold, and the S1 DVD uses a silver/copper alloy as its reflective layer (Table 2). ToF-SIMS analysis also suggests that metal-containing dyes, perhaps phthalocyanines, are used in the write layers. AFM measurements of the DVD grooves show that their physical dimensions are all different, and among all of the DVDs, grooves of the A3 and A4 DVDs are quite close to one another, consistent with the similarities of their chemical compositions. See summary of results in Table 2. These differences in the discs may ultimately influence their lifetimes.

Table 2. The plastic substrates, adhesives and reflective layers' chemical compositions of the A1-4 and S1 DVDs.

	A1	A2	A3	A4	S1
Plastic substrate	Polycarbonate	Polycarbonate	Polycarbonate	Polycarbonate	Polycarbonate
Adhesives	Acrylate-based	Acrylate-based	Acrylate-based	Acrylate-based	Acrylate-based
Reflective layer	Gold	Gold	Silver w/ gold on the back	Silver w/ gold on the back	Silver/copper alloy

REFERENCES

[1] McFarland, Patrick, "How to choose CD/DVD archival media", http://adterrasperaspera.com/blog/2006/10/30/how-to-choose-cddvd-archival-media, Oct 30, 2006.

[2] Perenson, Melissa J., "Burning questions: picking the right media, part 2", http://www.pcworld.com/article/120833/burning_questions_picking_the_right_media_part_2.html, May 17, 2005.

[3] Shim, Richard, "Try scratching this DVD", http://news.cnet.com/Try-scratching-this-DVD/2100-1041_3-5455621.html, November 17, 2004.

[4] Lunt, Barry M., Linford, Matthew R., "Towards a true archival-qulity optical disc," Proceedings of ISOM 2009 (International Symposium on Optical Memory); Nagasaki, Japan, Oct 4-8, 2009.

[5] Tsai, M., Lee, Y., and Long, Y., "Synthesis of a polydimethylsiloxane-block-hydroxyl grafted acrylate prepolymer copolymer to improve the adhesion between silicone rubber and polyurethane by induced surface reconstruction," Journal of Polymer Research 7 (2), 73-79 (2000).

[6] Ragauskienė, D., and Makuška, R., "Consolidation and ageing features of vinylneodecanoatecontaining in adhesive films used as a support for museum textiles," CHEMIJA 17 (2–3), 52–59 (2006).

[7] Bauer, B., Flyunt R., Czihal, K., Langguth H., Mehnert R., Schubert R., and Buchmeiser M.R., "UV curing and matting of acrylate coatings reinforced by nano-silica and micro-corundum particles," Progress in Organic Coatings 60, 121–126 (2007).

[8] Stephan, T., "ToF-SIMS in cosmochemistry," Planetary and Space Science 49, 859–906 (2001).

[9] Hurditch, R.J., "Stabilized dye compositions for optical recording media," US Patent 6,077,584 (2000).

[10] Wei, B., Wu Y., Gu D. and Gan F., "Optical and thermal properties of nickel-azo dyes for digital versatile disc-recordable," Chinese Phys. Lett. 20, 1517 (2003).

[11] Mustroph, H., Stollenwerk, M. and Bressau, V., "Current Developments in Optical Data Storage with Organic Dyes," Angew. Chem. Int. Ed. 45, 2016 – 2035 (2006).

[12] Beyrich, J., et al, "Metallocenyl phthalocyanines as optical recording media," US Patent 7378221 (2008).

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