Surface Modification of Steel Foils by Depositing Cr/Al or Al/Cr Thin Films: Effect of Rapid Heat Treatment

Received 28 June, 2021; revised 8 September, 2021; accepted 9 September, 2021

Hayk Khachatryan^a, Kyoung-Bo Kim^{b,*}, and Moojin Kim^{c,*}

^aDepartment of the Materials Technology and Electronics, Russian-Armenian University, Yerevan 0051, Armenia

^bDepartment of Metallurgical & Materials Engineering, Inha Technical College, Incheon 22212, Republic of Korea

^cDepartment of IoT Electronic Engineering, Kangnam University, Yongin 16979, Republic of Korea

*Corresponding author E-mail: kbkim@inhac.ac.kr, moojinkim7@kangnam.ac.kr

ABSTRACT

In this study, Al and Cr films were deposited onto steel substrates, and the film growth and microstructure were tracked. In the first set of experiments, Al was directly deposited onto steel, and Cr films were then deposited on top of the formed Al films. In the second set of experiments, it was *vice versa*; that is, Cr films were deposited onto the steel substrate, followed by Al film deposition. This technique was aimed at controlling the reflection property of the steel substrate to enable using steel foils for flexible display fabrication. It was observed that temperature significantly influenced grain formation and growth processes. When the temperature reached 550 °C, segregation occurred in the system where Cr contacted the steel, and Al was on the top layer. However, a similar phenomenon was not observed in the steel/Al/Cr system. The reflection value significantly decreased from 92 to 5–7 %, owing to these segregations.

Keywords: Al, Cr thin film, Steel-metal interface, Grain growth, Agglomeration, Surface treatment

1. Introduction

Electronic devices have been extensively used in different areas. In particular, devices with displays have attracted considerable attention. Therefore, the display industry has received significant investments, leading to several new and innovative technologies. Among these technologies, organic light-emitting diode (OLED) displays exhibit excellent performance and have become critical players in the market within a short period [1–3]. The next stage in evaluating electronic devices is the development of a flexible or rollable concept [4,5]. In this case, a flexible substrate is used instead of a rigid substrate, and thus, it is possible to fabricate a truly flexible display. A substrate material suitable for electronic applications must satisfy several requirements, including high flexibility, high thermal stability, dimensional stability (particularly at high temperatures), low water vapor, low oxygen transmission rate, and low surface roughness. Currently, three main types of flexible substrates can satisfy these requirements: i) thin metals, ii) ultrathin glass (UTG) [6, 7], and iii) plastics, such as polyimides [8, 9].

Each material has its peculiar advantages and disadvantages. Plastic substrates, particularly transparent plastic substrates, exhibit good optical transmittance similar to that of thin glass, and they have good flexibility; however, they possess poor dimensional stability, low process temperature, and weak chemical resistance. Their water and oxygen transmission rates are significantly high. UTG has excellent optical properties, very low water oxygen transmission rates, good chemical resistance, and excellent thermal and dimensional stability; however, it exhibits poor mechanical performance, that is, it is brittle. The metal alloy, Invar, has high dimensional stability and flexibility, and

its mechanical properties are similar to those of stainless steel. Invar has extremely low water and oxygen transmission rates. Invar foil is highly attractive to the display industry as a substrate for fabricating flexible display devices [10]. However, the metal substrate has poor surface smoothness and is highly reflective.

During display fabrication, it is critical to optimize the optical performance of the display device to provide improved picture quality. A major issue related to optical performance is the “color washing” effect. Thus, an OLED display device contains pixels consisting of a thin-film transistor, electrodes (cathodes and anodes), and an emissive layer. Top-emitting displays typically include a mirror (thin silver film) layer under the anode layer to enhance emission in the output direction. However, ambient light also passes through all layers and is reflected by the mirror layer. This phenomenon significantly reduces the contrast. Hence, the stack is thoroughly designed and optimized to overcome this problem. Additionally, placing a circular polarizer on top of the display stack causes the ambient light to become circularly polarized inside the device, for example, right-handed. Subsequently, the reflected light is cut off by the same polarizer. Despite its outstanding optical performance, the polarizing film increases display stack stiffness and decreases the device flexibility. In addition, it cuts almost 50 % of light. Consequently, poll-less technology has been developed, in which the polarizer layer is replaced with a color filter and a black matrix [11]. Poll-less reflection from the substrate is a critical issue that needs to be addressed.

As explained above, the Invar foil exhibits excellent performance and can be utilized as a high-end substrate for flexible display fabrication. However, the high reflection that may cause color deterioration can be a limitation; hence, a method that overcomes this challenge is

highly required from an industrial viewpoint. In this study, we developed a surface treatment method to solve steel substrate reflection. In particular, the thin-film deposition technique was applied to modify the surface composition and morphology. To change the surface composition, we selected metals that could form intermetallic compounds with Invar, thus changing the reflection. The deposition conditions were controlled to alter the surface morphology and decrease reflection.

2. Experimental details

The metallic films, that is, Al and Cr, were deposited using dual sputtering equipment. The equipment had two target parts operated using direct current (DC) and resonant frequency (RF) power: the upper and lower electrodes, a vacuum chamber, a sample holder, and a power controller. Al was deposited using DC, and Cr was deposited using RF. The substrate steel was placed on the sample holder, and the chamber was vacuumed to $\sim 1 \times 10^{-4}$ Torr. A DC power of 1000 W and an RF of 300 W were applied to the electrode at room temperature to form Al and Cr thin films, respectively. The distance between the metal target and the substrate was 20 cm. The substrate was rotated at 5 rpm to obtain a uniform coating. Under the selected conditions, the estimated deposition rates of the Al and Cr layers were 4.5 and 1.7 Å/s, respectively.

We investigated two types of structures. For the first type, we first deposited Cr onto the steel substrate and then deposited Al on top of the Cr. The Cr and Al layer thicknesses were adjusted to 10 and 150 nm, respectively. For the second type, the Al (150 nm) film was first deposited, followed by Cr film deposition (10 nm).

After depositing the films on the top of the substrates, the assembled components were heat-treated at 150, 350, and 550 °C. For this purpose, we used a rapid thermal annealing furnace. The heating rate was 8.5 °C/s. The samples were maintained at each target temperature for 20 min. After annealing, the furnace was switched off, and the samples were cooled naturally.

The microstructures and film thicknesses of the deposited films were evaluated using scanning electron microscopy (SEM, Carl Zeiss Merlin, Germany). Atomic force microscopy (AFM, SPA-300HV SII, Japan) was applied to scan the morphologies of the films and substrates. Sheet resistance was measured using the four-probe method (MSTECH, Korea), surface reflection was measured using a spectrometer (JASCO, Japan).

3. Results and discussion

It is well known that the growth, structure, and properties of a deposited thin film significantly depend on several factors such as (1) the nature of the substrate, (2) substrate temperature, (3) deposition rate, (4) contamination, and (5) presence of defects on the substrate surface. In our previous study, we demonstrated that the performance and properties of deposited Al thin films are significantly dependent on the substrate type [12]. Depositing a 150 nm Al film yielded crystalline and cross-grained films. In another study, we observed that the crystal size of the Al film depended on the film thickness, and crystallinity significantly influenced the optical properties. We estimated that depositing a 100 nm Al film on a steel substrate increased the reflection from 60 to 90%. However, a further increase in the Al film thickness resulted in decreased reflection (80%) because of the grain growth and rough surface formation. Although some improvements were observed, the remaining reflection was still significant [13].

To improve the optical performance, we added a thin Cr layer between the Al and steel.

Based on the phase diagram of the Fe-Cr binary system in the 1:1 ratio case, metastable σ -FeCr could be stabilized. The content of this component could attain 60 wt% by mass [14]. The compound was

stable up to 280 °C, from which it started to transform into bcc-FeCr. Cr_2O_3 was formed on top of the surface when the annealing temperature exceeded 450 °C.

Thus, we expected that the formation of FeCr and chromium oxide might modify the surface properties. It can be expected that this new property will be unchanged up to 450 °C because no significant variations in the phase state occur. However, when the annealing temperature exceeded 450 °C, it was expected that the surface properties would change significantly.

Furthermore, formations of intermetallic compounds, such as Al_7Cr , Al_4Cr , $\text{Al}_{11}\text{Cr}_4$, AlCr , and AlCr_2 , were expected [15]. The composition of the formed intermetallic material depends on the ratio of the metals. It can be assumed that Cr-rich intermetallic compounds are formed closer to the interface. The gradual structure may enhance diffusive scattering.

The SEM images of the Al/Cr/steel assembly are shown in Fig. 1. Figure 1(a) shows the reference substrate surface, and Fig. 1(b) shows the as-deposited film. These types of morphology and crystalline structure were observed in our previous study, in which the grain growth mechanism and the thickness effect of the film structure were demonstrated [13]. It was believed that the Al film deposition onto the metallic substrate occurred in three stages: i) condensation and nucleation, ii) coalescence, and iii) channeling. In the first stage, nuclei were formed and grew to form primary grains. Next, secondary nucleation occurred, and an integral film was formed. These two grains had different structures. It was estimated that film formation through this mechanism resulted in a cross-grained structure.

A similar structure was observed when Al was deposited onto Cr, and the primary and secondary grains were well distinguished (Fig. 2). It is expected that surface roughness will increase. We performed AFM analyses of the Al/Cr thin film samples before and after deposition to confirm this hypothesis (Fig. 3). Based on the results, the roughness (RMS) values of the steel substrate were 11.4 nm before deposition but increased up to 45.0 nm after Al/Cr film deposition.

As mentioned above, in Al/Cr and Cr/Fe systems, several intermetallic compounds are formed at different temperatures. Thus, the formed interlayers may induce different effects on the reflection values. To verify this possibility, we measured the optical properties of

Figure 1. SEM images of (a) reference substrate surface and (b) as-deposited Al/Cr/steel film. The inset of (b) is an actual image of Al/Cr/steel.

Figure 2. SEM image of Al/Cr/steel assembly.

Figure 3. AFM images of (a) steel substrate and (b) surface of Al/Cr/steel assembly.

the films. The reflection values of the samples are shown in Fig. 4. It was observed that the reference substrate had approximately 60–75 % reflection, whereas after Al/Cr layer deposition, the reflection reached up to 90 %. Similar behavior was observed for the samples annealed at 350 °C. However, the reflection significantly decreased when the annealing temperature reached 550 °C. It is well known that the incident light can be reflected in the specular direction or be diffusely scattered independent of the incident direction. The former is predominant in polished metallic surfaces, whereas rough surfaces reflect nearly all incident lights diffusely [16]. Surface roughness plays a key role in the relative ratio of specular to diffuse reflectance. Theoretical models predicting this behavior have been established. One of the earliest and most well-recognized models is the Torrance–Sparrow model, which reflects a direct physical connection between a rough surface and its visual appearance [17]. In this model, the reflectance is based on geometrical optics; therefore, the model is valid only when the surface is rough (has sufficiently large facets) compared to the wavelength of the incident radiation.

The grain sizes of the deposited thin films were similar in the wavelength range of visible light (Figs. 1 and 2). One can expect that the contribution of diffusive reflection would increase; hence, the reflection value should be lower than that of the reflection of the reference foil. Surprisingly, this was not the case. A phase diagram of each system must be considered to clarify this phenomenon. From the Al–Cr phase diagram, no significant changes were observed when the temperature was below 650 °C. When the temperature exceeded 650 °C,

Figure 4. Reflection spectrum of steel substrate before deposition of Al/Cr layers (reference) and after deposition (as-deposited), annealed at 150, 350, and 550 °C.

Figure 5. SEM images (a) annealed at 150 °C, (b) 350 °C, and (c) 550 °C. The insets are the actual images of heat-treated Al/Cr/steel samples.

other compounds were formed. In our study, a new Cr–Al intermetallic layer was not formed when this system was annealed at temperatures lower than 650 °C. Unlike the Al–Cr system, sedimentation of Cr_2O_3 and structural changes occurred in the Cr–Fe system when the temperature exceeded 450 °C. This transformation may have significantly decreased the reflection. Increasing the CrOx ratio in the Cr–CrOx bilayer film decreases the reflection, and the reflection decreases to 3.82 % when the CrOx reaches 40 % [18].

To confirm the assumption that sedimentation is essential for decreasing reflection, we performed SEM analyses of the annealed samples (Fig. 5). Annealing at 350 °C did not significantly influence the

Figure 6. AFM images of the Al/Cr/Steel samples (a) as-deposited, (b) annealed at 150 °C, (c) 350 °C, and (d) 550 °C.

morphology, but above 500 °C, the morphology changed significantly. The AFM analyses also supported this result, indicating that the surface morphology underwent significant changes when the annealing temperature exceeded 500 °C (Fig. 6). The AFM data for all the samples are listed in Table I. Samples annealed up to 350 °C showed similar roughness, but the Al/Cr/steel sample annealed above 550 °C showed considerably different roughness.

Table I. Roughness values of samples.

	RMS roughness (nm)
Al/Cr/Steel (as-deposited)	45
Al/Cr/Steel (annealed at 150 °C)	49.2
Al/Cr/Steel (annealed at 350 °C)	46.2
Al/Cr/Steel (annealed at 550 °C)	258.1
Cr/Al/Steel (as-deposited)	53.8
Cr/Al/Steel (annealed at 150 °C)	44.5
Cr/Al/Steel (annealed at 350 °C)	49.1
Cr/Al/Steel (annealed at 550 °C)	58.9
Steel substrate	11.4

Figure 7. Sheet resistance of Al/Cr/steel assembly before and after annealing.

A phenomenon was observed when the sheet resistance was measured. The sheet resistances of the thin films and reference substrate are depicted in Fig. 7. The sheet resistance of the steel was 0.027 Ω·cm, but when we deposited the thin film, the resistance increased up to 7 times and reached 0.178 Ω·cm. However, after annealing, the sheet resistance decreased, and a higher annealing temperature decreased the sheet resistance. For films annealed at 550 °C, the sheet resistance reached an initial value of approximately 0.027 Ω·cm.

The annealing temperature may directly influence the sheet resistance if the film contains a mixture of phases and the volume fraction of those phases changes with temperature [19]. It was expected that increasing the temperature might change the composition of the intermetallic compounds without significantly influencing the surface morphology. When the temperature exceeded the sedimentation temperature, the sheet resistance attained its initial value.

In summary, the main factors influencing the reflection values are i) the formation of Cr-Fe intermetallic compounds and ii) the sedimentation and formation of Cr₂O₃. To confirm this hypothesis, we examined the reverse structure, that is, Al was deposited onto the steel surface followed by Cr film deposition. In this case, there was no contact between Fe and Cr; hence, the formation of the Fe-Cr intermetallic

Figure 8. SEM (left) and AFM (right) images of (a) as-deposited Cr/Al/steel sample, annealed at (b) 150 °C, (c) 350 °C, and (d) 550 °C.

Figure 9. SEM images of Cr/Al/steel samples: (a) as-deposited and (b) annealed at 350 °C and (c) 550 °C.

compound was excluded. Figure 8 shows the SEM images of the films annealed at 150–550 °C. No significant changes in morphology were observed.

However, slight sedimentations/drops appeared on the surface of the sample annealed at 550 °C (Fig. 9). The morphology was similar when the annealing temperature reached 350 °C, but consolidation and sedimentation were observed when the temperature reached 550 °C. These phenomena were expected to influence the optical properties. The reflection increased when a film was deposited onto top of the steel substrate (Fig. 10). However, the increased values are significantly lower than when the Al film was on top. Thus, the reflection was approximately 90 % when Al was on the outermost top layer, but when Cr was the topmost layer, the reflection was 60–75 % (slightly higher than that of the pure steel substrate, which is approximately 55 %). The same value was measured in [20] for Cr films.

Similar to the previous system, annealing decreased the reflection values. Hence, the samples annealed at 550 °C had decreased reflection values of 20–30 %, which could be attributed to the formed chromium oxide layer. However, the reflection value was not as low as that of the Al/Cr/steel system when intermetallic compounds were formed (Fig. 4).

Figure 10. Reflection spectrum of steel substrate before deposition of Cr/Al layers (reference) and after deposition (as-deposited), annealed at 150, 350, and 550 °C.

4. Conclusion

In this study, Al/Cr films were deposited onto steel to improve the optical performance of steel substrates. In the first case, Cr was deposited onto the steel, and the Al film was deposited onto the top of the Cr film. In the second case, Al was directly deposited onto the steel, and a Cr film was formed on top of the Al film.

The Al film deposition on Cr/steel occurred in three stages. Consequently, well-formed primary grains and small secondary grains were formed. The formation of these grains increased the roughness value by approximately 40 %.

In the first case, when Cr and Al were deposited and the Al/Cr/steel assembly was formed, the reflection value increased from 60 to 90 %. However, the annealing of these samples at temperatures above 550 °C decreased the reflection value to 5–7 %. This behavior was linked to the formation of intermetallic compounds and chromium oxide. Thus, in the Cr-steel system, the formed sigma-FeCr was transformed to bcc-FeCr when the annealing temperature exceeded 280 °C. For annealing at 450 °C, Cr₂O₃ was formed, owing to Cr surface segregation. Consequently, the reflection values decreased significantly.

In the second case, when Al was deposited onto the steel and then a Cr film was formed on top of the Al, the reflection value increased by approximately 20–30 %, reaching 75 %. Annealing at 550 °C decreased the reflection, but this decrease was insignificant compared to that of the Al/Cr/steel system.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2021R1F1A1046135).

Conflict of Interest

The authors declare no conflicts of interest.

ORCID

Hayk Khachatryan
Kyoung-Bo Kim
Moojin Kim

<https://orcid.org/0000-0002-3420-7435>
<https://orcid.org/0000-0002-5863-3164>
<https://orcid.org/0000-0002-3626-3465>

References

- [1] B. Geffroy, P. I. Roy, and C. Prat, *Polym. Int.* 55, 572 (2006).
- [2] N. Sain, D. Sharma, and P. Choudhary, *Int. J. Eng. Appl. Sci. Technol.* 4, 587 (2020).
- [3] M. Kodan, *OLEDs Displays and Lighting* (Wiley-IEEE Press, Hoboken, 2016), pp. 124-146.
- [4] T. Amazawa, E. Yamamoto, and Y. Arita, *IEEE Trans. Electron Devices* 45, 815 (1998).
- [5] R. Yao *et al.*, *Material* 10, 222 (2017).
- [6] D. Nieto, F. Cambronero, M. T. Flores-Arias, N. Farid, and G. M. O'Conno, *Opt. Lasers Eng.* 88, 233 (2017).
- [7] G. S. Rohrer *et al.*, *J. Mater. Sci.* 52, 9819 (2017).
- [8] C. S. Oh, J. S. Bae, S. H. Choa, and H. J. Lee, *Proceedings of the 13th International Conference on Experimental Mechanics*, edited by E. E. Gdoutos (Alexandroupolis, Greece, July 1-6, 2007), pp. 61-62.
- [9] G. Kaune, E. Metwalli, R. Meier, V. Körstgens, K. Schlage, S. Couet, R. Röhlberger, S. V. Roth, and P. Müller-Buschbaum, *ACS Appl. Mater. Interfaces* 3, 1055 (2011).
- [10] Y.-Q. Xiong, X.-C. Li, Q. Chen, W.-W. Lei, Q. Zhao, L.-J. Sang, Z.-W. Liu, Z.-D. Wang, and L.-Z. Yang, *Chin. Phys. B* 21, 078105 (2012).
- [11] D.-H. Kim and B.-Y. Kim, *J. Electrochem. Soc.* 148, C10 (2001).
- [12] S.-J. Hwang, W. D. Nix, and Y.-C. Joo, *Acta Mater.* 55, 5297 (2007).
- [13] K. T. Raić, *Surf. Eng.* 32, 823 (2016).
- [14] M. Gich, E. A. Shafranovsky, A. Roig, A. Ślowska-Waniewska, K. Racka, L. I. Casas, Yu. I. Petrov, E. Molins, and M. F. Thomas, *J. Appl. Phys.* 98, 024303 (2005).
- [15] K. K. Raina, T. Zhang, and A. McTeer, *U.S. Patent 6,348,403 B1* (1999).
- [16] B. van Ginneken, M. Stavridi, and J. J. Koenderink, *Appl. Opt.* 37, 130 (1998).
- [17] K. E. Torrance and E. M. Sparrow, *J. Opt. Soc. Am.* 57, 1105 (1967).
- [18] S.-F. Wang, H.-C. Lin, H.-Y. Bor, Y.-L. Tsai, and C.-N. Wei, *J. Alloys Compd.* 509, 10110 (2011).
- [19] J. J. G. P. Loo, *Nucleation and growth of PVD aluminum* (Philips Electronics, Amsterdam, 1998), pp.1-29.
- [20] I. V. Gorbov, D. Yu. Manko, A. A. Kryuchyn, Zichun Le, Minglei Fu, and A. V. Pankratova, *Metallofiz. Noveishie Tekhnol.* 38, 267 (2016).