Structural-Color-Control by AlN Coating on Rough-Surface Al Film

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The surface roughness of the rf-sputtered Al film has been controlled by using a method of two steps deposition at two different substrate temperatures (473 K and 300 K). One of the Al films with a proper surface roughness shows low specular reflection and high diffuse reflection in visible region, and looks like white colour without gloss. When a transparent (50-400 nm thick) AlN film is deposited on the roughened Al film, its color is changed into wheat, light-skyblue, khaki, and light-plum depending on the AlN film-thickness. It is revealed that the major part of the whole reflection from the specimen is diffuse reflection due to the surface roughness, and the variety of color without gloss is caused by the interference effect by the deposition of AlN film.

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1. Introduction

Decorative coatings have important role in the coloration of various industrial products.¹⁾ One of the methods of coloring coatings is application of intrinsic optical property of coating material. For example, one of the most typical decorative coatings is titanium-based decorative coating, which shows color variation depending on the composition of TiN,²⁾ TiO₂,³⁾ TiC, TiCN,⁴⁾ TiCNO,⁵⁾ etc. Another coloring coating method is based on the interference effect by the transparent coating. For example, TiN film coated with transparent SiO₂ layer shows color variation depending on the thickness of SiO₂.⁶⁾ Such type of decorative coating is usually applied on the optical flat surface. Therefore, the coloring depends on the viewing angle of an observer, in other words, it colors near the condition of specular reflection.

On the other hand, recently we discovered the black colored Al-N films caused by the surface roughness.⁷⁾ Furthermore, it is well known that the gloss of Al film is lost by its surface roughness. Therefore, an interference effect on the surface roughness using a transparent coating is examined in this study. This coloration is a kind of structural colors. In the natural world more complex structural color exists, e.g., some butterfly wings with structural combination of arrangement of concavities in micron scale and multilayer thin-film structure.^{8,9)} First of all, the experimental condition to form the Al film with a proper surface roughness, which gives high diffusive reflectance in visible region, is investigated. Then, an effect on the coloring of the transparent AlN coating on this rough-surface Al film is examined.

2. Experimental

Films were deposited by using rf sputtering apparatus, which was evacuated by a turbo-molecular pump. The base pressure was 5×10^{-5} Pa. A water-cooled 100-mm-diameter Al target (99.999%) was sputtered. The mixture of Ar

(99.9995%) and N₂ (99.999%) or the pure Ar was used as sputtering gas. The total working gas pressure (P_{tot}) was 1.33 Pa, which was the sum of the partial pressure of N₂ (P_{N_2}) and that of Ar. In order to change the composition of the film, the concentration of partial N₂ gas pressure ($c_{\text{N}_2} = 100 \times P_{\text{N}_2} / P_{\text{tot}}$) was changed. Transparent AlN film was obtained at $c_{\text{N}_2} = 12\% \text{N}_2$.⁷⁾ Of course the pure Al film was formed without N₂. Corning #7059 glass (0.7 mm in thickness) was used as a substrate. Film thickness was measured using a surface texture measurement instrument (Surfcom 200B, Tokyo Seimitu Ltd.). The deposition rates were estimated by using smooth films with the thickness less than 100 nm. The typical deposition rates at input power of 200 W were 0.18 and 0.13 nm/s at 0 and 12%N₂, respectively. Then in this study each film (or layer) is named by its substance, deposition film thickness (d) which is estimated by deposition rate, and substrate temperature (T_{sub}), e.g., a notation of Al(d , T_{sub}) represents an aluminum film with a thickness of d deposited at T_{sub} .

Surface morphology was observed using an atomic force microscope (AFM: Nanopics, NPX100AFM head, Seiko Instruments Inc.). Optical properties of the specimens were measured using an ultraviolet-visible-near infrared spectrometer (UV-3100PC, Shimadzu Co.) in the wavelength range of 0.24 to 2.60 μm . The specular reflectance (R_0) was evaluated by measuring the reflectance at an incidence angle of 12°. The diffusive reflectance (R_d) at normal incidence was also measured using an integrating sphere with a diameter of 60 mm. The color photograph of specimen is taken using a digital camera (Digital Revio KD-300Z, Konica Co.).

3. Results

In this study, a method of two steps deposition of Al layer at two different substrate temperatures is adopted, i.e., first Al layer with the thickness of d_1^{Al} is deposited at 473 K, then second Al layer with a thickness of d_2^{Al} ($=300 \text{ nm} - d_1^{\text{Al}}$) is deposited at 300 K without breaking vacuum. The total thickness of Al film for visible reflector is fixed to be 300 nm, because the transmittance of 300 nm-thick Al film is experimentally negligible small. Let us express this type of

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Fig. 1 Film thickness of lower Al reflector (d_1^{Al}) dependence of (a) specular reflectance (R_0) and (b) diffusive reflectance (R_d) of the specimen of Al(300 nm- d_1^{Al} , 300 K)/Al(d_1^{Al} , 473 K)/glass.

stacking layers as 'Al(d_2^{Al} , 300 K)/Al(d_1^{Al} , 473 K)/glass' in this paper hereafter.

The surface roughness and the diffusive reflectance of the Al(d_2^{Al} , 300 K)/Al(d_1^{Al} , 473 K)/glass are controlled by d_1^{Al} . The d_1^{Al} dependence of R_0 and R_d are shown in Figs.1(a) and (b). In these figures, $d_1^{\text{Al}} = 0$ nm corresponds to Al(300 nm, 300 K)/glass. This specimen has a flat surface and shows specular reflection, *i.e.*, large R_0 (Fig.1(a)) and small R_d (Fig.1(b)) in a wide observed wavelength region (0.24–2.60 μm). In relatively shorter wavelength region, R_0 decreases (Fig.1(a)) and R_d increases (Fig.1(b)) with increasing d_1^{Al} . The increase in R_d seems to compensate for the decrease in R_0 . A specimen of Al(100 nm, 300 K)/Al(200 nm, 473 K)/glass is chosen to be the substrate for the transparent AlN coating, since this specimen shows the large value of R_d (about 0.8) in the visible region. The corresponding bird's eye view AFM image is shown in Fig.2(a). Its full-width at half-maximum (FWHM) of the distribution of relative frequency of the height along the surface normal (DRFH) is 275 nm and the standard deviation (σ) is 91 nm.

The transparent AlN film with a thickness (d^{AlN}) from 50 to 400 nm is deposited on the reflector of Al(100 nm, 300 K)/Al(200 nm, 473 K)/glass at 300 K without breaking vacuum. An example of surface morphology of AlN(d^{AlN} =400 nm, 300 K)/Al(100 nm, 300 K)/Al(200 nm, 473 K)/glass is shown in Fig.2(b). Over all feature of the AlN coated surface (Fig.2(b)) is similar to the uncoated surface (Fig.2(a)). FWHM and σ of DRFH of the 400 nm-thick AlN coated surface decrease slightly to 253 nm and to 86 nm respectively. It has been confirmed that the surface roughness does not change seriously up to the 400 nm-thick AlN deposition.

However, the optical properties are systematically changed. The d^{AlN} dependence of R_0 and R_d of AlN(d^{AlN} , 300 K)/Al(100 nm, 300 K)/Al(200 nm, 473 K)/glass are shown in Figs.3(a) and 3(b). The effect of AlN coating on R_0 does not strongly appear in visible region, but in infrared region. And furthermore, the effect of AlN coating also appear in the oscillation of R_d in visible region as shown in

Fig. 2 Bird's eye view AFM images of (a) Al(100 nm, 300 K)/Al(200 nm, 473 K)/glass and (b) AlN(400 nm, 300 K)/Al(100 nm, 300 K)/Al(200 nm, 473 K)/glass.

Fig. 3 AlN film thickness (d^{AlN}) dependence of (a) specular reflectance (R_0) and (b) diffusive reflectance (R_d) of AlN(d^{AlN} , 300 K)/Al(100 nm, 300 K)/Al(200 nm, 473 K)/glass. Dashed lines are reflectance spectra of AlN(100 nm, 300 K)/Al(300 nm, 300 K)/glass with optical flatness.

Fig.3(b). R_0 and R_d of the specimen with relatively flat surface are shown by dashed lines in Figs.3(a) and (b) for comparison. Its specimen is AlN(100 nm, 300 K)/Al(300 nm, 300 K)/glass whose σ of DRFH is less than 4 nm. Corresponding R_0 shows oscillation in visible region (Fig.3(a)) and R_d is negligible small (Fig.3(b)). Then it has been noticed that the appearance of interference effect in R_d is a characteristic of the rough-surface specimen.

As mentioned in the previous section, the R_d has been measured at normal incidence. Considering its reverse optical path, it is deduced that a structural color caused by the surface roughness can be seen by a diffusive lighting from surroundings. In order to demonstrate this, a simple attempt has been made. The specimens are illuminated with conventional fluorescent lights diffusively reflected by white papers, which

Fig. 4 Appearance of specimens. (a) AlN(100 nm, 300 K)/Al(300 nm, 300 K)/glass with flat surface. (b), (c), (d), (e), and (f) are AlN(d^{AlN} , 300 K)/Al(100 nm, 300 K)/Al(200 nm, 473 K)/glass with d^{AlN} =0 nm, 50 nm, 100 nm, 200 nm, and 400 nm respectively.

surround the specimens to cover their semi-solid angle. Then a photograph of Fig.4 is taken from near surface normal. A metallic ruler is stood perpendicularly to the surface of the specimens. The flat specimen is shown in Fig.4(a) as a reference. The image of the ruler is clearly reflected in the specular surface with a color of light skyblue. The specimen of Fig.4(b) is the as deposited Al substrate with the surface roughness as shown in Fig.2(a). Its color is white and no image of the ruler can be seen. Then after depositing AlN, in response to the change of 50 nm, 100 nm, 200 nm, and 400 nm in d^{AlN} , the color of specimen of AlN(d^{AlN} , 300 K)/Al(100 nm, 300 K)/Al(200 nm, 473 K)/glass changes to wheat, light-skyblue, khaki, and light-plum, as shown in Figs.4(c), (d), (e), and (f). In these rough-surface specimens, the image of ruler is hardly reflected in the surface. The change in the color corresponds to the optical properties in visible region as shown in Figs.3(a) and (b). As a result it is confirmed that the coloration of the specimen with surface roughness is also possible.

4. Conclusion

In this study, one of the structural colors had been realized for the first time by using the surface roughness of the sputtered Al. The roughness was controlled by the substrate temperature. Then as deposited Al(100 nm, 300 K)/Al(200 nm, 473 K) film showed large diffusive reflectance (about 0.8) in visible region. Its color looked like white without gloss. Furthermore, by covering with the transparent AlN, its color changed variously depending on the AlN-thickness. It was confirmed that a reason of coloring was interference effect, which appeared in the diffusive reflectance in the case of the specimen with the proper surface roughness.

In this experiment only one kind of Al template of the surface roughness had been examined. However, if we use different form and/or degree of surface roughness, the diversity of the color will be expected. And furthermore, present type of structural color also seems to be preferred from a viewpoint of environmental issue because the film does not include any poisonous pigment but consists of only Al and N. In these senses, the application in the field of the industrial decorative coating and/or the arts and crafts is expected.

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