Formation of Transparent Aluminum Hydroxide Film with Mesoscopic Surface Roughness by Hydrothermal Treatment of Incompletely-nitrided Sputtered Aluminum Film

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Abstract. Incompletely-nitrided Al films (Al-N film) are deposited on the glass substrate by rf sputtering with a metallic Al target and using Ar and N₂ gas mixture. With increasing film thickness up to 300nm, the surface roughness increases. And the roughness is easily controlled. The size and the number density of surface protuberance are suitable to control diffusive optical properties in the visible and near infrared regions. The films become transparent with retained roughness by boiling in ultra pure water at 368K under atmospheric pressure. The films have been transformed from composite of Al and AlN to aluminum hydroxide (Boehmite). Total transmittance of the boiled specimens exceeded that of the glass substrate itself. These facts suggest that hydrothermally-treated Al-N films with the mesoscopic surface roughness have high potential to reduce the optical loss by reflection.

1. Introduction

Full-fledged use of environmentally friendly energy, especially use of solar energy has been starting to prevent greenhouse warming. In the first place, solar energy is one of the energy resources with thin energy density. Therefore, we have to improve not only efficiency of solar cell itself but also reduction of optical loss due to reflection from the cell, which occurs essentially at surface and/or interface with abrupt change in refractive index.

In order to realize a structure of a kind of optical-matching, we use MgF₂ and CaF₂ etc., because their refractive index is around 1.4, which is one of the median values of 1.6 of glass and 1 of air. Or more specifically, surface with mesoscopic roughness plays a role of the gradient-refractive index. We have reported that the surface structure of Al and/or Al-N films is one of proper candidates [3-5]. Recently, we succeeded in transforming of Al and Al-N films from opaque to transparent one, which is useful for anti-reflective coating [6, 7]. This is quite simple method, i.e., just boiling the films in the ultra pure water, by which Al and Al-N films transform into aluminium hydroxide film.

In this study, we examine the controllability of the surface roughness for the Al-N films. Then, evaluation of transparent films by boiling has been performed systematically.
2. Experimental

Al-N films were deposited on 0.70mm-thick Corning 7059 glass substrate by using rf sputtering method. An Al target (99.999%, 100mm diameter) was sputtered in the mixture gas of Ar (99.9995 %) and N\textsubscript{2} (99.9995 %) with a concentration of 7.3 vol\%N\textsubscript{2}. The working gas pressure was 1.33 Pa. The input rf power was 200W. The substrate temperature (\(T_{\text{sub}}\)) was 373K. Film thickness (\(d_f\)) was changed from 100nm to 300nm.

As deposited Al-N films were boiled in stirred ultrapure water at 368K under atmospheric pressure. Ultrapure water with a resistivity of higher than 18.0 M\(\Omega\cdot\)cm was used. Boiling time was chosen from 2 min to 20 min depending on the film thickness.

Surface morphology was observed using an atomic force microscope (AFM: Nanopics, NPX100, Seiko Instrument Inc.). The optical properties were measured using an ultraviolet-visual-near infrared spectrometer (UV-3100PC, Shimadzu Co.) in the wavelength range of 0.24 to 2.60 \(\mu\)m. Specular reflectance (\(R_0\)) was evaluated by measuring the reflectance at an incidence angle of 12°. Diffusive reflectance (\(R_{\text{dif}}\)) was measured using an integrating sphere with a diameter of 60mm. The incident light energy (=1) is the sum of the total transmittance (\(T_{\text{tot}}\)), total reflectance (\(R_{\text{tot}}\)) and absorbance (\(A\)). \(T_{\text{tot}}\) is the sum of forward transmittance (\(T_0\)) and diffusive transmittance (\(T_{\text{dif}}\)). \(R_{\text{tot}}\) is the sum of \(R_0\) and \(R_{\text{dif}}\). Then, the rule of energy conservation is represented by 1 = \(T_{\text{tot}} + R_{\text{tot}} + A = T_0 + T_{\text{dif}} + R_0 + R_{\text{dif}} + A\).

In order to distinguish the incidence direction to a specimen having the film / substrate structure, the superscript of fil for the incidence on film surface or the superscript of sub for the incidence on substrate will be used, if necessary.

3. Results and Discussion

Figure 1 shows the difference in appearance of as-deposited Al-N films with different thickness and their change by boiling in water. With increasing film thickness, metallic surface (Fig. 1(a)) becomes blackened surfaces (Figs. 1(b) and (c)). After boiling, they change into transparent films as shown in Figs. 1(d), (e) and (f).

Optical properties of as-deposited opaque Al-N films are shown in Fig. 2. \(R_0\) decreases with \(d_f\). On the other hand, \(R_{\text{dif}}\) increases with \(d_f\) at longer wavelength region. And the peak position of \(R_{\text{dif}}\) seems to be shifted toward longer wavelength with \(d_f\). Then, \(R_{\text{tot}}\) decreases with \(d_f\). These facts mean that thicker Al-N film shows excellent light absorption properties in the visible and near infrared region [4].

![Figure 1](image-url)  
Figure 1. Appearance of as-deposited Al-N films with different film thickness on Corning #7059 glass substrate. (\(T_{\text{sub}} = 373K\)) (a) \(d_f=100nm\). (b) 200nm. (c) 300nm. Each film becomes transparent (d), (e), and (f) after boiling at 368K for 2 min, 9 min, and 20 min, respectively.
Optical properties of boiled specimens are shown in Fig. 3. As seen in Fig. 3(a), $T_0$ decreases with $d_f$ at around visible region. $T_{\text{tot}}$ of the boiled specimens exceeded that of the glass substrate itself (Fig. 3(b)). Then, $T_{\text{dif}}$ is estimated by assuming zero absorption ($A=0$). As seen in Fig. 3(a) again, $T_{\text{dif}}$ increases to compensate the depression of $T_0$. In Fig. 3(c) and (d), $R_0$, $R_{\text{dif}}$ and $R_{\text{tot}}$ corresponding to Figs. 1(d), (e), and (f) are also shown. With increasing $d_f$, $R_0$ decreases and $R_{\text{dif}}$ increases. Then, $R_{\text{tot}}$ falls below values of glass substrate. These optical properties, i.e., higher $T_{\text{tot}}$ and lower $R_{\text{tot}}$, are quite useful property for the AR coating.

**Figure 2.** Film thickness dependence of specular reflectance ($R_0$) (a), diffusive reflectance ($R_{\text{dif}}$) (b) and total reflectance ($R_{\text{tot}}$) (c) for as-deposited Al-N films.

**Figure 3.** Film thickness dependence of (a) specular transmittance ($T_0$) and diffusive transmittance ($T_{\text{dif}}$), (b) total transmittance ($T_{\text{tot}}$), (c) specular reflectance ($R_0$) and diffusive reflectance ($R_{\text{dif}}$), and (d) total reflectance ($R_{\text{tot}}$). For comparison, optical properties of glass substrate are also shown.
AFM observation of the change in the surface morphology by boiling is shown in Fig. 4. Surface roughness increases with $d_f$ (Figs. 4(a)-(c)). After boiling, surface roughness changes from Figs. 4(a), (b), and (c) into Figs. 4(d), (e), and (f). A tendency of increasing surface roughness with $d_f$ can be seen. In addition, the width of each protuberance seems to grow.

In order to characterize the surface morphology, the root-mean-square (RMS) roughness and the areal number density of surface protuberance ($N_{pro}$) are estimated as shown in Fig. 5 from AFM images of Figs. 4. In the case of RMS roughness, difference between before and after boiling is not so large. It increases linearly with the film thickness for $d_f > 100$nm. In other words, surface roughness of as-deposited film is rapidly enhanced above $d_f=100$nm. On the otherhand, $N_{pro}$ is seen to decrease by a factor of about 2, which means protuberance’s growth in lateral direction takes place. Then, it could be mention that the degree and/or size of surface roughness can be controlled by initial Al-N film thickness.

Figure 4. Bird’s eye view AFM images of as-deposited (a) 100nm-thick, (b) 200nm-thick, and (c) 300nm-thick specimens and those of after boiling ((d), (e), and (f)). Here, (d), (e), and (f) corresponds to (a), (b), and (c).

Figure 5. Film thickness dependence of the root-mean-square (RMS) surface roughness and the areal number density of surface protuberance ($N_{pro}$). Comparison between as-deposited film and boiled film is also shown.
Finally, complex refractive indices of \( n - ik \) is calculated by using optical data observed for boiled 30nm-thick specimen, which is specially-deposited at 293K to get a flat surface. Obtained values are almost same as the values for boiled Al film, which is described in our former paper [7]. Therefore, it is mentioned that \( n \) of boiled Al-N film or Boehmite film also shows intermediate values between glass and air. This is thought to be another reason for low reflectance.

![Complex refractive indices](image)

**Figure 6.** Calculated complex refractive indices of \( n - ik \) for boiled Al-N film and Corning #7059 glass.

### 4. Conclusion

We confirmed that the Al-N films with mesoscopic surface roughness were reformed to transparent films by hydrothermal treatment. Their surface roughness of the boiled Al-N film could be controlled by \( d_f \) of as deposited Al-N film. After hydrothermal treatment, with increasing surface roughness, \( T_0 \) decreases and \( T_d \) increases. However, \( T_{tot} \) for all of the specimens increases beyond \( T_{tot} \) of the glass substrate itself in all of wavelength ranges.

Complex refractive indices \( (n - ik) \) of the boiled Al-N film were calculated. Its refractive index \( (n) \) is around 1.3, which is one of the median values of 1.6 of glass and 1 of air.

These results indicate that the boiled Al-N film with mesoscopic surface roughness is useful for the AR coating such as solar cell and/or other optical devices.

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