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Spectroscopic Ellipsometry Study of Thin Film of Gold Iodide with Stearylammonium

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Spectroscopic ellipsometry has been used to examine the refractive index changes by a photoirradiation of the hybrid thin film consisting of gold iodide and stearylammonium iodide. The measurements are performed in the wavelength range of 270–1650 nm at room temperature. It is found that the significant change of refractive indices occurs in the near infrared region, though the film was almost transparent in that region.

Keywords: hybrid thin film; gold iodide; spectroscopic ellipsometry; photo-reduction

INTRODUCTION

Some gold iodide compounds have been much expected as the material for the optoelectronic device. Kojima et al. measured polarized reflectance spectra of $Cs_2Au^{I}Au^{III}I_6$ single crystal which is a perovskite-type compound with the mixed-valence state of gold cations.[1] This crystal had an intervalence charge transfer spread in two-dimensionally delocalized field of gold-to-iodide networks, and was expected as a material for the optoelectronic device. However, it is relatively difficult to fabricate into a thin film with high transparency. We already succeeded to fabricate the gold iodide with a long alkyl chain into a thin film by the conventional spin-coating technique.[2]

It has been essential for the development of optoelectronic devices to control the optical properties of the material. For this purpose, it is very important to know the refractive index and the absorption coefficient with accuracy. Spectroscopic ellipsometry is a superior technique to investigate the optical constants such as a refractive index of the material in the shape of thin film.

In this study, we have examined a structural change of the gold iodide thin film induced by photoirradiation, and estimated the refractive indices using spectroscopic ellipsometry. Obtained results are discussed from the viewpoints of the correlation to molecular structures.

EXPERIMRNTAL

Gold triiodide (AuI_3) and stearylammonium iodide (SAI) were dissolved in acetonitrile solution ([AuI_3]=0.140 mol/l, [SAI]=0.146 mol/l). The thin films were made on a quartz substrate by a conventional spin-coating technique. The solution was dropped onto the substrate and spread with the spinning rate of 3500 rpm. A photoirradiation to the film was performed by 500 W Xenon lamp. The partly masked film was placed in front of the lamp house. The film was photo-irradiated for about 2 hours without any filter or lens.

Absorption spectra of the films were taken by Shimadzu UV-3100 spectrophotometer in the wavelength range of 200-2400 nm. Spectroscopic ellipsometry measurements were performed by Jobin-Yvon UVISEL spectroscopic phase modulated ellipsometer in the 270-1650 nm wavelength range at room temperature. Classical dielectric function ε was used for the fitting.

$$\varepsilon = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)\omega_t^{\,2}}{\omega_t^{\,2} - \omega^2 + i \cdot \Gamma_0 \cdot \omega}$$

where ε_∞ is a high frequency dielectric constant, ε_s a static frequency dielectric constant, ω_t an angular transverse frequency and Γ_0 a damping factor for single oscillator.

RESULTS AND DISCUSSION

An obtained film was highly transparent with a reddish purple color. Figure 1 shows an X-ray diffraction profile of the SAI-AuI_3 thin film. Four sharp peaks were observed at 2θ=2.75, 5.50, 8.25, and 11.05°. This periodic diffraction profile may indicate that the hybrid film forms a layered structure with perpendicularly oriented long alkyl chains. Its layer spacing is estimated as

32.1Å.

In Figure 2(a) the solid line shows the absorption spectrum of the SAI-AuI_3 thin film. Four absorption bands were observed at 288, 370, 537, and 694 nm. All bands are assigned to the ligand-to-metal charge transfer transition in the AuI_x^- (x=2, 4).[3, 4] Especially, strong 537 and 694 nm bands are characteristic to the AuI_4^-. The longer wavelength region than 1000 nm was well transparent. This spectral pattern was extremely changed by photoirradiation. The observed spectrum is shown in Fig. 2(a) (broken line). Four strong bands reduced their intensities. The obtained spectral pattern was quite similar to that of AuI_2^-. Such a spectral change could not be obtained by simple heating. Therefore, the phenomena can be attributed to the photo-reduction of gold ion from Au^{3+} to Au^{1+}.

We corrected spectroscopic ellipsometry data of the thin films before and after the photoirradiation. Their fitting results on the refractive indices were shown in Figure 2(b). It was found that the significant difference of refractive indices occurred not only in UV-visible region but also in near infrared region, in

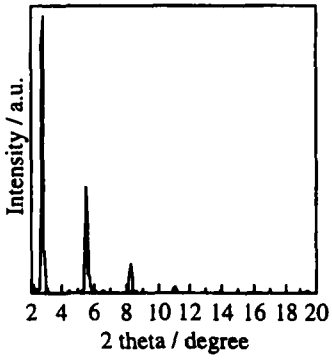

FIGURE 1 X-ray diffraction profile of SAI-AuI_3 thin film.

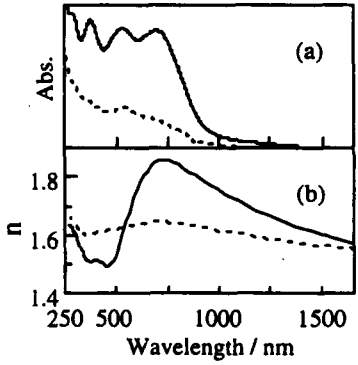

FIGURE 2 Absorption spectra (a) and refractive indices spectra (b) of SAI-AuI_3 thin film (solid line) and photoirradiated film (broken line).

which their absorption coefficients were nearly equal to zero. The differences in the refractive index ($\Delta n/n$) were 4.30% at 1.3μm and 2.28% at 1.55μm.

From the analogy of other AuI_4^- compounds,[5] it is suggested that (-Au-I-I-Au-) zigzag chain structure with the delocalized electric field exists in this hybrid thin film before the photoirradiation. No network structure with delocalized electrons in the solid state was reported in the case of AuI_2^- compound. It seems that the network of Au^{III}–I was broken by photoirradiation, which induce the reduction from Au^{3+} to Au^+. Therefore it is suggested that the difference between their refractive indices is concerned with delocalized electrons in the gold-iodide network.

CONCLUSION

We have examined refractive index changes of the gold iodide thin film induced by photoirradiation. It was found that more than 4.30% of refractive index changes would be observed in the near infrared region, although this region was quite transparent for both films before and after the irradiation. The finding that the control of refractive index is possible in the near infrared region with no absorption bands would be applicable to the waveguide material.

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