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Aluminium Oxide Optical Film Fabricated with Ion-Assisted Deposition Using Sulphur Hexafluoride and Oxygen Working Gases

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Al_2O_3 thin films fabricated by electron-beam evaporation with ion-assisted deposition at room temperature using O_2 or SF_6, or their mixture as a working gas were investigated. A significant 20% packing density increase and a low extinction coefficient were obtained when only SF_6 was used. © 2011 The Japan Society of Applied Physics

Keywords: Al_2O_3, ion-assisted deposition, optical properties, packing density, SF_6

1. Introduction

The wavelength of the light source used in microelectronic industry during lithographic processes becomes shorter as narrower line widths are required in semiconductor chips, such as KrF excimer laser (248 nm) and ArF excimer laser (193 nm) which are widely used. However, high-refractive-index materials with low absorption in the deep UV region are rare.[1–4)] Al_2O_3 thin films with a high refractive index and stable chemistry are good transparent materials in the mid, deep UV regions. However, non-stoichiometic Al_2O_3 films[5)] with a porous structure easily react with the atmospheric moisture such that the films' properties deteriorate with time. Hence, the improvement of film packing density is crucial to the film durability. Since fluorine has the highest electro negativity among all the elements, extra bonds are expected between aluminium and fluorine once fluorine is introduced into Al_2O_3 structure, which will result in a film with a higher packing density. In this work, Al_2O_3 films were deposited by electron-beam evaporation with ion-assisted deposition (IAD) at room temperature using O_2, or SF_6 or their mixture in an attempt not only to increase film packing density but also to obtain a low extinction coefficient at optical wavelength (λ) of 266 nm.

2. Experiment

Prior to mounting the sample onto the sample holder and pumping down the system, fused silica substrates were cleaned using methonal in an ultrasonic cleaner and blown dry using nitrogen gas. The vacuum chamber was pumped down to a base pressure of 6×10^{-6} Torr. Then, the working gas of a laboratory-made end-Hall ion source was filled with O_2 or SF_6, or their mixture until the total chamber pressure reached 2.0×10^{-4} Torr. Before the deposition, the substrate was cleaned with plasma from the ion source. The thickness and the deposition rate of the film monitored using a quartz crystal were ~3000 Å and 1.5 Å/s, respectively. The transmittance spectra of as-deposited Al_2O_3 thin films were measured using a spectrophotometer (Varian Cary 5E). The refractive index, extinction coefficient, and thickness were measured by spectroscopic ellipsometer (VASE; J. A. Woollam M-2000U). The chemical compositions of the films were analyzed by both Fourier transform-infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS).

3. Result and Discussion

The transmittance spectra of the Al_2O_3 films deposited using oxygen as the sole working gas at various ion-beam voltages are shown in Fig. 1. The total pressure of the chamber was maintained at 2.0×10^{-4} Torr and an ion-beam current of 0.75 A. The extinction coefficient is smaller and the transmittance is highest for the film deposited at an applied ion-beam voltage of 120 V in the wavelength range from 190 to 600 nm.

Once the optimum ion-beam voltage was determined, 120 V, the films were deposited at different ion-beam currents of 0.75, 1, 1.25, and 1.5 A. In Table 1 the refractive indices and the extinction coefficients measured by spectroscopic ellipsometry using the Cauchy model and the calculated packing densities of the films fabricated under various conditions are listed. Packing density was calculated from the FTIR results using the equation below,[6)]

$$P = 1 - \frac{\ln(T_0/T)}{\alpha_w d_f}, \quad (1)$$

where P is the packing density, α_w is the water absorption coefficient at $1.27 \times 10^{-4}\,\text{cm}^{-1}$, T is the transmittance of the film in air, T_0 is the transmittance of the film in vacuum, and d_f is the thickness of the film.

The film with the highest refractive index at a fixed ion-beam current of 0.75 A was found as the applied ion-beam voltage was 120 V. When the ion-beam voltage was increased from 100, 120 to 140 V, the extinction coefficient of the films increased. This may be attributed to not only film damage caused by the bombardment of energetic ions but also water adsorption during film deposition. The water

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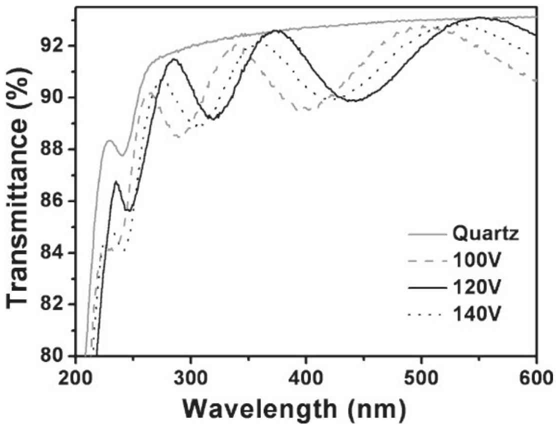

Fig. 1. Transmittance spectra of the Al_2O_3 films fabricated using oxygen as a working gas at various ion-beam voltages.

Table 1. Optical properties of Al_2O_3 films at $\lambda = 266$ nm fabricated under various conditions with oxygen as the sole working gas.

Parameters of IAD (V/A)	Refractive index	Extinction coefficient	Packing density (%)
100/0.75	1.638	5.6×10^{-3}	70.9
120/0.75	1.679	8.7×10^{-3}	71.4
140/0.75	1.637	1.1×10^{-2}	71.0
120/1.00	1.651	7.5×10^{-3}	69.7
120/1.25	1.652	6.0×10^{-3}	71.8
120/1.50	1.697	7.2×10^{-3}	71.4

absorption peak in the film was clearly seen in the FTIR spectra shown in Fig. 2, especially in the case of using O_2 as the sole working gas. When the ion-beam voltage was fixed at 120 V with the current increasing from 1.00, 1.25 to 1.50 A, the highest packing density with the lowest extinction coefficient was found in the film prepared at 1.25 A. However, a lower refractive index was detected in this film. The highest refractive index but a higher extinction coefficient was observed in the film prepared at 1.50 A. Since films with the highest packing density and lowest extinction coefficient were the major concerns in this study, the deposition parameters of the films prepared with IAD were set at 120 V and 1.25 A. Regardless of the current or voltage were applied during the Al_2O_3 film fabrication at a total pressure of 2.0×10^{-4} Torr the highest packing density of all the films was only 71.8%.

In order to understand how the optical properties of the Al_2O_3 film vary as a function of total gas pressure used during the deposition, the other total pressure of 1.0×10^{-4} Torr was also used when the working gas was only oxygen. It was found that the optical properties and the packing density of the film deposited at 1.0×10^{-4} Torr are better than those of the film deposited at 2.0×10^{-4} Torr, as shown in Table 2. Although the packing density 72.4% obtained at 1.0×10^{-4} Torr is higher than that 71.8% obtained at 2.0×10^{-4} Torr, it is not high enough for the applications of optical thin films. Since fluorine has the

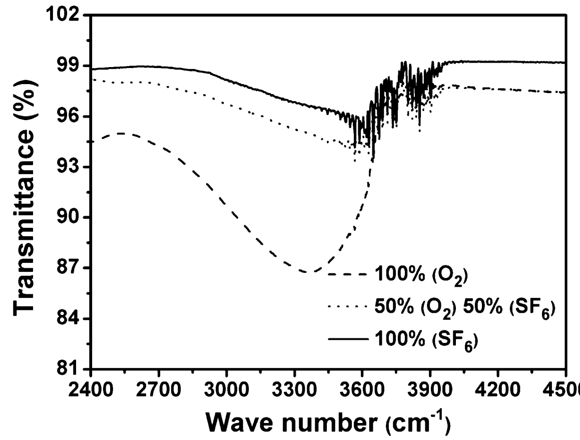

Fig. 2. FTIR spectra of the films fabricated using O_2 or SF_6, or their mixture as a working gas.

Table 2. Optical properties of Al_2O_3 films at $\lambda = 266$ nm fabricated under different pressures of oxygen working gas.

Pressure of working gas (Torr)	Refractive index	Extinction coefficient	Packing density (%)
2.0×10^{-4}	1.652	6.0×10^{-3}	71.8
1.0×10^{-4}	1.714	5.2×10^{-3}	72.4

Table 3. Optical properties of the Al_2O_3 films at $\lambda = 266$ nm fabricated by using O_2 or SF_6, or their mixture as a working gas.

Working gas	Refractive index	Extinction coefficient	Packing density (%)
100% (O_2)	1.714	5.2×10^{-3}	72.4
50% (O_2) + 50% (SF_6)	1.582	3.6×10^{-3}	89.5
100% (SF_6)	1.539	3.1×10^{-3}	92.3

highest electro negativity among all the elements, extra bonding is expected between aluminium and fluorine once fluorine is introduced into Al_2O_3 structure, which will result in a film with a higher packing density. Therefore, a working gas mixture of O_2 and SF_6 was used in order to further increase film packing density. The ratios of SF_6 to O_2 in the working gases were 0, 50, and 100%, respectively. From the FTIR spectra shown in Fig. 2, the water absorption peak in the film decreases significantly and the packing density increases up to 92.3% with the increase in SF_6 gas proportion as listed in Table 3.

The lowest extinction coefficient and the highest packing density are obtained for the sample prepared using only SF_6 as the working gas, but the refractive index of the sample is lowest among the samples, as shown in Table 3. A low refractive index of fluorinated Al_2O_3 is expected due to the low polarizibility of the electrons from fluorine. The compositions of O, F, S, and Al in this film (in atomic %) obtained by XPS are 33.01, 25.06, 2.58, 32.82%, respectively. The concentration ratio of F to S in the film is about 10 to 1, which indicates that more F and less S are deposited in the film. It was observed that the more SF_6 in the working gas, the higher the packing density of the film, which confims that extra bonding is indeed established between aluminium and fluorine once fluorine is introduced into the Al_2O_3 structure.

4. Conclusions

Al_2O_3 thin films were deposited by electron-beam evaporation with IAD at room temperature under various deposition conditions using O_2 or SF_6, or their mixture as a working gas. It was confirmed that fluorinated Al_2O_3 film containing a very high packing density of 92.3% was achieved in this work owing to the high electro negative fluorine in the film. However, a low refactive index of fluorinated Al_2O_3 film is inevitable owing to the electrons tightly bonded to fluorine in the film. Because of the highly packed film and newly formed chemical bonds in the Al_2O_3 film containing fluorine, a significant improvement in the extinction coefficient, 3.1×10^{-3}, is obtained. This work shows that the packing density, extinction coeffient, and refractive index of Al_2O_3 films can be tailored by introducing an appropriated concentration of fluorine into the films.

Acknowledgements

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