Fabrication of amorphous Al$_2$O$_3$ optical film with various refractive index and low surface roughness

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Abstract

Alumina(Al$_2$O$_3$) thin film has been widely used in many applications due to its excellent properties, especially in optical films and semiconductor industries. Refractive index, amorphous property and surface roughness are essential parameters related to its applications. In this study, the fabrication method of preparing various refractive index Al$_2$O$_3$ optical films was proposed. The Al$_2$O$_3$ optical films were deposited at room temperature by electron beam evaporation (EBE) technique. The effects of deposition rate and post-annealed temperature on refractive index, vibration peak of molecular and atom, amorphous property and surface roughness were investigated. Refractive index ranging from 1.519 to 1.627 was realized by EBE method at different deposition rates and different post-annealed temperatures. The variable refractive index was very important in adjusting half-width of reflector band. Meanwhile, analysis showed that the suitable post-annealed temperature could not exceed 400 °C. In short, this work provided an effective approach to fabricate amorphous Al$_2$O$_3$ optical film, which was pretty important in its applications in UV antireflection films and blue light reflection films.

1. Introduction

Alumina(Al$_2$O$_3$) thin film has been widely used in many fields, especially in optical films and semiconductor industries, such as cavity coating, gate oxide in metal oxide semiconductor field effect transistors (MOSFET), passivation or moisture barrier layer in solar cells, protective layer and hydrophobic layer [1, 2]. Good surface adhesion property, high melting point, high crystallization temperature, good chemical stability and compatibility with semiconductor process are significant qualities for its applications [3–5]. Al$_2$O$_3$ optical film has been prepared by different techniques based on chemical vapor method and physical vapor method, such as chemical vapor deposition (CVD) [6], atomic layer deposition (ALD) [7, 8], electron beam evaporation (EBE) [9, 10] and so on. The uniform and reproducible Al$_2$O$_3$ optical film with controlled thickness can be fabricated by ALD and EBE methods. Al$_2$O$_3$ optical films have various refractive indices, such as 1.51, 1.6, 1.63, 1.66 ~ 1.77, 1.63 ~ 1.69, 1.61 ~ 1.66, 1.65 ~ 1.69 and 1.70 ~ 1.74 [11–18]. However, refractive indices fabricated by EBE method are all higher than 1.66 according to the current reports [11, 12, 14, 19]. Refractive index of Al$_2$O$_3$ film is higher than that of low refractive index SiO$_2$ film. And refractive index of Al$_2$O$_3$ film is lower than that of many high refractive index films such as Ta$_2$O$_5$, HfO$_2$, ZnSe and TiO$_2$ films. So Al$_2$O$_3$ optical film is widely used to create mirrors such as bandpass filters, antireflection coatings and high reflection coatings [5, 11, 20]. The theory of light wave interference indicates that half-width of reflector band is only determined by high and low refractive index value. And 0.01 deviation in refractive index will lead to tens nanometers migration at half-width of reflector band. Al$_2$O$_3$ optical film with low refractive index has been prepared by ALD method successfully, but it has not been realized by EBE deposition method based on the existing reports. EBE is a widely used film deposition mode in film applications. So it is difficult but vital important to fabricate various refractive index Al$_2$O$_3$ optical film by this method.
In this paper, the Al$_2$O$_3$ optical films with the refractive indices ranging from 1.519 to 1.627 were fabricated by EBE method. The effects of deposition rate and post-annealed temperature on refractive index, film thickness, vibration peak of atoms and molecules, film crystallinity and surface morphology were investigated. These results were very important for the application of Al$_2$O$_3$ optical films. It is an important low refractive index film in deep UV reflection films and an important high refractive index film in blue light reflection films.

2. Material and methods

Al$_2$O$_3$ optical films were deposited on SiO$_2$/Si(100) substrates by Leybold ARES710 EBE coating machine. The Si substrates had a polished and oxidized SiO$_2$ insulation layer. And the purity of Al$_2$O$_3$ grain was 99.9%. Orthodontic plate and turntable that rotated at a certain speed were used to reduce thickness error during deposition process. All the substrates were posited on a concentric circle to ensure the film uniformity. Cold well was used to promote vacuum degree and shorten vacuum drainage time. EBE method could effectively accelerate deposition rate, extend sputtering time, reduce cost and enlarge sputtering area.

The preparation process could be summarized as the following steps. Firstly, Si substrate was cleaned by acetone, absolute ethyl alcohol and deionized water in order for 10 min. Secondly, chamber vacuum was evacuated to $4.0 \times 10^{-4}$ Pa before deposition. Thirdly, substrates were cleaned by plasma under the same deposition conditions for 120 s to remove the impurities on the substrates. Fourthly, film thicknesses of all samples were 300 nm controlled by a crystal vibration measurement system. Finally, samples(a1-Al$_2$O$_3$ ~ a5-Al$_2$O$_3$) were prepared by varying deposition rate and samples(b1-Al$_2$O$_3$ ~ b5-Al$_2$O$_3$) were prepared by varying post-annealed temperature(details in table 1). Post-annealed process was accomplished in an OTF-1200X oxidation furnace for 2 h.

3. Results and discussion

3.1. Refractive index and thickness analysis

The refractive index of Al$_2$O$_3$ thin films was measured by spectroscopic ellipsometry(SE, J A Woollam EC-270). The influences of deposition rate and post-annealed temperature on refractive indices were shown in figures 1(a) and (b). The refractive indices of Al$_2$O$_3$ films were shown in figure 1(a) when the deposition rate was in the range of 0.1 nm s$^{-1}$ ~ 0.5 nm s$^{-1}$. And figure 1(b) showed the refractive indices of Al$_2$O$_3$ films while the post-annealed temperature increased from 100 °C to 500 °C. The refractive index decreased as the optical wavelength increased, which was consistent with the former reports but lower than the reported value. As shown in figure 1(a), the refractive indices of Al$_2$O$_3$ film at 940 nm were 1.564, 1.593, 1.588, 1.584 and 1.582, when the deposition rate was 0.1 nm s$^{-1}$, 0.2 nm s$^{-1}$, 0.3 nm s$^{-1}$, 0.4 nm s$^{-1}$ and 0.5 nm s$^{-1}$, respectively. It first increased, reached a maximum value of 1.593 when the deposition rate was 0.2 nm s$^{-1}$, and then decreased as the deposition rate further increased. The reason was that greater deposition rate promoted more energy to electron gun and beam. As a result, more energy was given to ions and atoms under high energy beam conditions. The Al$_2$O$_3$ particles had high energy and could migrate and repair on the substrate surface at high deposition rate [21, 22]. The Al$_2$O$_3$ film density was increased with the increase of deposition rate. The relationship between film density $p$ and film refractive index $n_f$ was defined as equation (1).

\[ n_f = n_v + p(n_v - n_i) \]

(1)
Where $n_A$ was the measured film refractive index, $n_t$ was the film refractive index in theory, $n_p$ was the refractive index of air (about 1), $p$ was the film density, $r_n$ and $r_s$ were constants [23]. According to these analyses, the refractive index of Al$_2$O$_3$ thin film increased with the increase of deposition rate. When the deposition rate further increased, high energy resulted in large grains, which led to the enlargement of the surface roughness. In addition, high deposition rate and low migration rate of ions and atoms easily resulted in more voids. Therefore, refractive index decreased when the deposition rate increased from 0.2 nm s$^{-1}$ to 0.5 nm s$^{-1}$.

In order to analyze the effect of post-annealed temperature on the refractive indices of Al$_2$O$_3$ films, the refractive index before and after post-annealed process was detected. As shown in figure 1(b), the refractive indices of Al$_2$O$_3$ films at 940 nm were 1.573, 1.554, 1.529, 1.519 and 1.518, when the post-annealed temperature was 100 °C, 200 °C, 300 °C, 400 °C and 500 °C, respectively. The refractive index first decreased and then gradually kept a constant with the increasing of post-annealed temperature.

Post-annealed process could increase film density which was useful in increasing film refractive index. However, the refractive index of Al$_2$O$_3$ thin film decreased with the increase in post-annealed temperature. The desorption process might be the main reason, which resulted in the decrease of Al$_2$O$_3$ thin films refractive index [21, 22]. The samples were all fabricated at room temperature, and more steam existed in the chamber. Therefore, there would be more steam filled in the deposited films. The refractive index of steam was higher than that of the air. The desorption process reduced the amount of the filled steam, so the film refractive index was reduced in a result. In order to validate this assumption, the chamber was first heated to 200 °C to remove the steam in it and then cooled to 25 °C to deposit Al$_2$O$_3$ thin films. The other fabrication parameters were consistent with a2-Al$_2$O$_3$. The relationship between refractive index and wavelength of the samples with and without chamber heated was shown in figure 2. The refractive index of Al$_2$O$_3$ thin films with chamber heated reached 1.627, which was 0.034 higher than that of the Al$_2$O$_3$ thin films without chamber heated at the wavelength of 940 nm.

3.2. Raman vibration peaks analysis

The vibration peak of Al$_2$O$_3$ thin films was confirmed by Raman spectroscopy to illustrate the existence of steam. In order to further analyze the spectrum of the Al$_2$O$_3$ thin films, the spectrum of the substrate was measured for comparison. Figure 3 showed the test results of the samples after post-annealed process, which was compared with that of the unannealed sample. The intensity of the peak at 519 cm$^{-1}$ had obvious Gaussian distribution spectrum as shown in figure 3, which verified the existence of the crystalline Si [24–26]. In addition, we noticed that there was less obvious peak at 304 cm$^{-1}$, which was also assigned to the vibration of the substrate [4, 15].

Except for the peaks of the substrate, the spectrum of the as-deposited Al$_2$O$_3$ thin films showed another three peaks at 434 cm$^{-1}$, 621 cm$^{-1}$ and 671 cm$^{-1}$. The intensity of the 434 cm$^{-1}$, 621 cm$^{-1}$ and 671 cm$^{-1}$ was very small, but very close to 428 cm$^{-1}$, 613 cm$^{-1}$ and 665 cm$^{-1}$. It might be due to the existence of γ-Al(OH)$_3$ in the Al$_2$O$_3$ thin films [27]. After post-annealed process, there was only one peak at 519 cm$^{-1}$, which was the peak of the Si substrate. That was to say there was no Al(OH)$_3$ structure existed in the films. The reason was that post-annealed process removed the steam in the film. Al(OH)$_3$ was formed due to the presence of steam, which was unstable and could be easily removed through post-annealed process. So the refractive index of Al$_2$O$_3$ thin films
decreased after post-annealed process. And Raman spectroscopy further illustrated that the desorption process led to the variation of the refractive index.

3.3. X-ray diffraction spectra analysis

The diffraction pattern of Al₂O₃ optical films was carefully examined by an Empyrean X-ray diffractometer (XRD) with a parallel beam. Figures 4(a) and (b) showed the XRD patterns of Al₂O₃ thin films fabricated at different deposition rates (a₁-Al₂O₃ ~ a₅-Al₂O₃) and post-annealed at various temperatures (b₁-Al₂O₃ ~ b₅-Al₂O₃). The Al₂O₃ optical films deposited by EBE method existed in an amorphous phase at 41.5° rather than polycrystalline phases, since no characteristic peaks were observed in the XRD patterns. The deposition rate and post-annealed process described in this study had no effect on the crystallization of the Al₂O₃ thin films. What was more, it was still not high enough to crystallize the Al₂O₃ films when the post-annealed temperature was 500 °C. Amorphous dielectric layer minimized the number of defect states, so as to improve the electric performance of devices by configuring its interface bonding. This was essential to enhance the interface quality and surface topography [11, 28, 29]. The Al₂O₃ films prepared in this paper met well with the application requirements especially in optical films and semiconductor industries.

3.4. Surface morphologies analysis

The surface morphologies of Al₂O₃ films annealed at different temperatures were examined by Agilent 5500 scanning probe microscope as shown in figures 5(a)–(f). The surface roughness values were 0.111 nm, 0.140 nm, 0.154 nm, 0.139 nm, 0.128 nm and 2.70 nm, at the post-annealed temperature of as-deposited, 100 °C, 200 °C, 300 °C, 400 °C and 500 °C, respectively. The surface roughness first increased and then decreased with the
increase of the post-annealed temperature. The main reason was that higher post-annealed temperature gathered more atoms together from available neighboring sites [27]. However, the Al$_2$O$_3$ films could be hardly used in optical films at the post-annealed temperature of 500 °C due to its large surface roughness. Total optical scattering of optical films was proportional to $\delta^2/\lambda^2$, where $\delta$ was the surface roughness, $\lambda$ was the central wavelength [30]. The larger the surface roughness value, the more the total optical scattering. Therefore, Al$_2$O$_3$ thin films could be hardly used in optical films when post-annealed temperature exceeded 400 °C. Furthermore, previous studies showed that higher surface roughness caused lower refractive index [27, 31], which further confirmed the relationship between refractive index and post-annealed temperature. Based on the results of the refractive index, Raman vibration peaks, crystalline phase, and surface roughness, the suitable post-annealed temperature was not higher than 400 °C.

4. Conclusions

The EBE method was successfully employed to prepare variable refractive index Al$_2$O$_3$ films at room temperature. The effects of deposition rate and post-annealed temperature on refractive index, raman vibration peaks, crystalline phase and surface roughness were studied comprehensively. The refractive indices of Al$_2$O$_3$ films deposited at different deposition rate and annealed at different temperature were investigated by SE. The refractive index value was changed from 1.519 to 1.627. SE analysis showed that the refractive index first
increased to 1.593 and then decreased to 1.582 with the increasing of the deposition rate. Meanwhile, the refractive index first decreased to 1.573 and then reached a constant value of 1.519 with the increasing of the post-annealed temperature. The Raman analysis also helped explained the variation of the refractive index. XRD tests showed that all Al2O3 films revealed an amorphous phase rather than polycrystalline phases. The amorphous phase property was vital important in optical film and semiconductor industry applications. Surface morphologies of Al2O3 films annealed at different temperatures showed a non-monotonous trend. The surface roughness analysis showed that post-annealed temperature should not exceed 400 °C for its application requirements. Al2O3 optical films fabricated by this method was particular important in UV antireflection films and blue light reflection films due to its variable refractive index, amorphous property and ultra low surface roughness.

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Conflicts of Interest

The authors declare no conflict of interest.

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