Optical thin film deposition with O\textsubscript{2} cluster ion beam assisted deposition

Noriaki Toyoda, Isao Yamada

Laboratory of Advanced Science and Technology for Industry, Himeji Institute of Technology

Abstract. O\textsubscript{2} gas cluster ion beam (O\textsubscript{2}-GCIB) assisted depositions were studied to form high quality Ta\textsubscript{2}O\textsubscript{5}, Nb\textsubscript{2}O\textsubscript{5} and SiO\textsubscript{2} films. The optimum irradiation conditions for Ta\textsubscript{2}O\textsubscript{5} and Nb\textsubscript{2}O\textsubscript{5} film depositions were the acceleration energy of 5 to 9keV and the cluster ion current density over 0.5µA/cm\textsuperscript{2}, respectively. The Nb\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} films deposited with O\textsubscript{2}-GCIB irradiations showed very uniform and dense structures without columnar or porous structures. Due to the significant surface smoothing effect of GCIB, the interface and top surface of Nb\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} multi-layer were quite flat. The interference filter deposited with O\textsubscript{2}-GCIB assist deposition was very stable and there was no shift of wavelength before and after environmental tests. As O\textsubscript{2}-GCIB is equivalently very low-energy ion beam and is able to deposit flat and dense amorphous films at low substrate temperature, it is suited to deposit multi-layered films where low-energy assisting ions are required.

INTRODUCTION

It has been getting important to provide high-quality thin films for optical communication devices. Optical film itself has very long history used for anti-reflection coating, dielectric mirror and so on. However, thin films multi-layered filters for optical communication requires precise control of uniformity, stability, flatness and stress. If films are porous or low-density, wavelength shift of optical filter will occur due to penetration of water into the films. As the number of layers of these filters is a few hundreds, it is also important to deposit flat films at low-temperature, low-energy conditions. Reducing the charge is also preferred to avoid micro-discharge which causes voids in the films. For the fabrication of narrow band optical filters, Ion beam assist deposition (IBAD), RF plasma ion assist deposition, sputtering deposition and ion plating deposition have been developed. However, still there are many problems to overcome such as radiation damage by high-energy ions, voids formation, surface roughness propagation to upper layer, and so on.

We've been proposing the gas cluster ion beam (GCIB) process to replace the conventional ion beam at low-energy region, such as surface smoothing of various materials [1,2], high-rate etching with reactive cluster ions [3], surface cleaning and ultra shallow ion implantations with B\textsubscript{10}H\textsubscript{14} ions [4]. Gas clusters are huge aggregates with several to thousands of atoms. As each atom in a cluster shares total acceleration energy, an ultra low energy ion beam with several eV/atom can be easily realized even though the total acceleration energy is keV range. Also, as the irradiated area with cluster ion becomes high-temperature and high-pressure conditions due to dense energy depositions in a local area, there are enhancements of chemical reactions near the surface, which realizes high-density films without heating the substrate itself.

Most interesting characteristic of cluster ion beams is that it enhances lateral motion of atoms on the surfaces. With this effect, gas cluster ion beam exhibits strong surface smoothing effect. As gas cluster ion realizes very smooth surface, multi-layers with very flat interfaces can be deposited. With conventional deposition techniques, surface roughness increases with increasing the number of layers. However, the roughness does not propagate to the upper layer with O\textsubscript{2}-GCIB assist deposition, which is preferable for multi-layered film depositions [5]. In addition to the controllable parameter of atomic or molecular ion
beam such as ion energy and ion current density, the cluster size dominates the energy deposition process.

So it is very interesting to employ gas cluster ion beams as assisting ions for thin film deposition because it will realize to deposit very smooth and high-density films at low-temperature. Also, as GCIB is a very low-charge process, it can reduce discharges on substrates. In this study, high-quality optical films, such as Ta$_2$O$_5$, Nb$_2$O$_5$ and SiO$_2$, were deposited with O$_2$ gas cluster ion beam (O$_2$-GCIB) assisted depositions. Film properties and structures were explored under various deposition conditions and environmental test were performed to study the stability of the interference filters.

**EXPERIMENT**

The O$_2$ cluster ion beam assisted deposition system is equipped with an electron beam evaporator and a gas cluster ion beam source. The detail of our cluster beam assist deposition system was already reported [5]. Basically, the construction of this system is based on an ion beam assisted deposition, however cluster ions with very low-energy per molecules are employed as assisting ions. O$_2$ neutral clusters are formed by supersonic expansions of high-pressure O$_2$-He mixing gas through a Laval nozzle into a vacuum chamber. From previous time of flight (TOF) mass spectrometry study, neither He cluster formation and incorporation in O$_2$ cluster beam was observed because of small inter-atomic force of He. The average cluster size of O$_2$ cluster ion beam was approximately 1000 to 3000 atoms/cluster measured with TOF. In the deposition chamber, neutral O$_2$ clusters were ionized by electron bombardments and were accelerated up to 10keV to a quartz substrates. O$_2$ cluster ion current density was 1.0µA/cm$^2$ at the target. Granular Ta$_2$O$_5$, Nb$_2$O$_5$ and SiO$_2$ were evaporated from electron beam evaporator with deposition rate of 0.1nm/sec. The pressure during depositions was below 1x10$^{-4}$Torr. Deposition rates were monitored by a quartz crystal rate monitor. Thickness of the films was also monitored with reflection type optical monitor. Target temperature was around 100°C due to radiations from the electron beam source. After deposition, transmittance spectra, surface morphologies, cross-sectional images were measured with a spectrometer, an atomic force microscope (AFM) and a secondary electron microscope (SEM). Stabilities of Nb$_2$O$_5$/SiO$_2$ multi-layer were studied from changes of transmittance spectra after boiling test (100°C, 5 hours) and high-humidity test (85°C, 85%, 250 hours).

**RESULTS AND DISCUSSIONS**

Figure 1 shows surface roughness of Ta$_2$O$_5$ films deposited without O$_2$-GCIB irradiation, with neutral O$_2$ cluster beam and with O$_2$-GCIB having 7keV total acceleration energy. In the case of the Ta$_2$O$_5$ film without O$_2$-GCIB irradiation, the average surface roughness was 1.7nm. From AFM images, there are many bumps and grains on the surface due to columnar structure of the film. Irradiation of O$_2$ neutral cluster beam did not improve the average surface roughness. However, in the case of 7keV O$_2$-GCIB irradiation, the average roughness significantly decreased down to 0.3nm. As the pressure in the deposition chamber was the same as the case with neutral O$_2$ cluster beam irradiation, it clearly exhibits that energetic O$_2$ cluster ion is required to form high quality films.

In GCIB processes, energy of each constituent atom (energy/atom) defines the physical phenomena that occur at bombarded areas. When the energy/atom of cluster ion is several hundreds of eV, ion implantation is dominant process, and when that is around several tens of eV/atom, sputtering of materials becomes significant. Below several eV/atom, adequate energy depositions are expected without causing significant damage or sputtering, which is desirable for thin film assist depositions. To study the energy dependence of O$_2$ cluster ion beams for film properties, O$_2$ cluster ion beams were irradiated at various acceleration energies at the same ion current densities.

Figure 2 shows the total acceleration energy dependence of refractive indexes and surface roughness of Ta$_2$O$_5$ films deposited with O$_2$-GCIB irradiations. The refractive index was measured at wavelength of 633nm, and the surface roughness was obtained from AFM measurement in 1µm squares of observation area. The thickness of Ta$_2$O$_5$ films and ion current density were 180nm and 160nA/cm$^2$, respectively. The acceleration energy was changed from 0 to 11keV, and that of 0keV represents a neutral...
O₂ cluster beam irradiation. The dotted line in figure 2 represents the data without O₂-GCIB irradiations. With increasing acceleration energy, the refractive index increased and had a maximum at 7keV. From transmittance spectra, there was no absorption of light and the extinction coefficient was below 1x10⁻⁷ or detection level at wavelength more than 300nm. Regarding to the surface roughness, it suddenly decreased at acceleration energy of 5keV and showed saturated value of 0.5nm. From this result, the optimum acceleration energy of O₂-GCIB is between 5 to 9keV.

Another important parameter in ion beam assisted deposition is ion current density or flux ratio of evaporated material and irradiating ions. Figure 3 shows ion current density dependence of refractive indexes and surface roughness of Ta₂O₅ films. The evaporation rate of Ta₂O₅ from electron beam evaporator was fixed at 0.1nm/sec. Also acceleration energy of O₂-GCIB was fixed at 7keV. Ion current density of 0 represents the result with neutral O₂ cluster beams.

In the case of neutral O₂ cluster beam assist deposition, the refractive index of Ta₂O₅ was the same as Ta₂O₅ film deposited without O₂-GCIB irradiations. However, with increasing the cluster ion current density, the refractive index gradually increased and showed saturated value at 2.2 at ion current density over 0.8µA/cm². In figure 3, the surface roughness suddenly decreased from 1.6nm to 0.6nm around the ion current density of 0.5µA/cm². In the case of SiO₂, the drop of the surface roughness was around 0.7µA/cm². Same experiments were also performed for Nb₂O₅ films with O₂-GCIB assist deposition, and similar tendency was observed. From these experiments, it was found that the required O₂ cluster ion current density is more than 0.5µA/cm².

To study the structure of films deposited with O₂-GCIB assist deposition, Nb₂O₅/SiO₂ interference filters were formed. Figures 4 (a) and (b) show cross-sectional SEM images of Nb₂O₅/SiO₂ interference filter formed (a) with or (b) without O₂-GCIB irradiations. The magnification was 70,000 and the bright layers represent Nb₂O₅ films and the dark layers SiO₂. This interference filter had 13 layers of Nb₂O₅ and SiO₂ films designed to have a center wavelength at 1.55µm. The thickness of Nb₂O₅ and SiO₂ were 174nm and 266nm, respectively. The Nb₂O₅ cavity layer (7th layer from the bottom) had a thickness of 348nm. The acceleration energy and O₂ cluster ion current density were 9keV and 2.0µA/cm², respectively. The deposition rate was 0.1nm/sec and the target was quartz substrate without anti-reflection coating on the backside.

In the case of depositions without O₂-GCIB irradiations shown in figure 4 (a), each layer was porous and there were many columnar structures. The interface between each layer was not smooth and large grains and particles were observed. The average roughness of these films measured with AFM was about 1.5nm. On the other hand, with 9keV O₂-GCIB assisted deposition shown in figure 4 (b), all the layers had very uniform structures and there was no porous

![Figure 2. Acceleration energy dependence of refractive index and average roughness (Ra) of Ta₂O₅ films deposited with O₂-GCIB assist deposition.](image1)

![Figure 3. Cluster ion current density dependence of refractive index and surface roughness (Ra) of Ta₂O₅ and SiO₂ deposited with 7keV O₂-GCIB assist deposition.](image2)

![Figure 4. Cross-sectional SEM images of Nb₂O₅/SiO₂ multi-layer without O₂-GCIB (a) and with 9keV O₂-GCIB (b).](image3)
or columnar structure. Also the interfaces and top surface were very flat with average roughness of 0.5nm. From X-ray diffraction spectrum, these films had complete amorphous structures. Transmittance spectra for this interference filter formed with O2-GCIB assist deposition showed 96% of transmittance at wavelength of 1.55µm. As there was no anti-reflection coating on the backside of quartz substrates and there was typically several percent of loss due to the reflection at the backside, the transmittance of 96% indicates that there was almost no absorption in this filter.

To verify stabilities of the Nb2O5/SiO2 films deposited with O2-GCIB assisted deposition, environmental tests were performed for interference filters shown in figure 5(a) and (b). At first, the filter was dipped in boiling water for 5 hours, and subsequently high-humidity test were carried out by placing these filters in a chamber that was kept at 85°C with humidity of 85% for 250 hours. Figure 5(a) shows transmittance spectra of Nb2O5/SiO2 filter deposited without O2-GCIB assist. In figure 5(a), transmittance spectra significantly moved almost 30nm after a boiling test. The high-humidity test was also carried out after the boiling test, however, the film had many wrinkles on its surface and it was unable to measure a transmittance spectrum. These wavelength shifts of spectra were caused by percolation and absorption of water inside films during these tests. It means that the film was coarse and very low-density. However, in the case of O2-GCIB assist deposition as shown in figure 5(b), there was no change in the transmittance spectra even after boiling and high-humidity tests. These results indicate that O2-GCIB assist deposition can form high-density films so that it is stable even after these environmental tests.

CONCLUSION

O2 gas cluster ion beam (O2-GCIB) assisted depositions were applied to deposit high quality optical films such as Ta2O5, Nb2O5, and SiO2. The optimum irradiation conditions of O2-GCIB were acceleration energy of 5 to 9keV and the cluster ion current density over 0.5µA/cm², respectively. From cross-sectional SEM images of Nb2O5/SiO2, the films deposited with O2-GCIB irradiation showed very uniform and dense structures without columnar or porous structures. Interface and top surface of Nb2O5/SiO2 multi-layer was quite flat with average roughness below 0.5nm. The interference filter deposited with O2-GCIB assist deposition was very stable and there was no shift of wavelength after environmental tests. It indicates that the films are very dense and uniform so that prevent percolation of water or moistures into the films. As O2-GCIB is equivalently very low-energy ion beam and is able to deposit flat and dense amorphous films at low substrate temperature, it is suited to deposit multi-layered films where low-energy assisting ions are required.

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REFERENCES