LIQUID CLUSTER ION BEAM PROCESSING OF TRANSITION METAL FILMS

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Abstract

Liquid cluster ion beams were irradiated on metal surfaces to examine the possibility of applying the liquid cluster ion beam technique to the processing of metal films. An apparatus combining a liquid cluster ion beam system and magnetron sputtering deposition system was constructed to perform the processing of metal films using liquid cluster ion beams without exposing to the air. The sputtering yields of tantalum, copper, and platinum induced by ethanol cluster ion beams were 87, 26, and 46 times higher than those by argon monomer ion beam at 500 eV, respectively. The sputtering yields of metal films kept in vacuum were also 2.9 to 3.5 times higher than those exposed to the air after deposition.

INTRODUCTION

Recently, the possibility of low-damage high-rate processing of semiconductor materials using liquid cluster ion beams was demonstrated [1, 2]. The surfaces of the semiconductors were deeply etched by the irradiation of liquid cluster ion beams such as ethanol and acetone cluster ion beams without receiving serious radiation damages. In addition to the usual irradiation effects induced by noble-gas cluster ion beams, the enhancements of the chemical reactions between the molecules comprising the cluster and atoms in the surface were considered as the origin of this high-rate etching. The enhancement of the chemical reactions was thought to be due to the extremely hot and dense reaction field formed by the impact of cluster ions onto solid surfaces [3, 4, 5].

Following the progress of spintronics, the demands for fine-processing of metal films were growing. Because of the extremely low vapour pressure of chlorides, it is well known that the reactive ion etching (RIE) rate for transition metals are much lower than that for semiconductors. The residue remained after the RIE is also the well-known problem. On the other hand, because of the hot and dense reaction field and introduction of momentum upon collision of liquid clusters with metal surface, the liquid cluster ion beam technique is one of the possible solutions to these problems. Thus, the irradiation effects of liquid cluster ion beams, such as ethanol cluster ion beams on metal films have been studied to examine the possibility of applying liquid cluster ion beam technique to the processing of metal films.

EXPERIMENTAL

Figure 1 shows a schematic diagram of the experimental setup. The liquid cluster ion beam system [6, 7] (upper part) was modified by installing a magnetron sputtering deposition system (lower right part) next to the irradiation part to realize a liquid cluster ion beam processing without exposing the prepared metal films to the air. The detail of the liquid cluster ion beam system was described elsewhere [6,7].

Figure 2: Schematic diagram of magnetron sputtering deposition system.
The ethanol cluster was produced by the adiabatic expansion method [8]. Ethanol was filled into the source container and heated to increase vapour pressure using a line hater attached on the outer wall of the container. The typical vapour pressure was 0.3 MPa. The vaporized ethanol was ejected to the vacuum chamber through a supersonic nozzle to produce clusters. The neutral ethanol clusters were ionized by electron ionization. The typical acceleration voltage ($V_e$) and current ($I_e$) of the electrons were 200 V and 200 mA, respectively. The ionized ethanol clusters were accelerated with the acceleration voltage ($V_a$) from 3 to 9 kV. The ethanol monomers and small clusters were eliminated by the retarding voltage method. This method is based on the phenomenon that the velocity of the nozzle flow is highly uniform, typically within 10% [8,9]. The initial kinetic energy of the ethanol cluster based on this phenomenon is 0.29 eV/molecule. Thus, we can eliminate the ethanol clusters smaller than the cluster size of approximately 100 by the retarding voltage ($V_r$) of 29 V. The typical retarding voltage applied in this study was 27 V. The transverse divergence of the beam was suppressed using an einzel lens, and the vertical position was fine-tuned by using an electrostatic deflector.

Table 1: Parameters for Magnetron Sputtering Deposition

<table>
<thead>
<tr>
<th>Target</th>
<th>Ta</th>
<th>Cu</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target purity</td>
<td>99.99 %</td>
<td>99.99 %</td>
<td>99 %</td>
</tr>
<tr>
<td>Target size</td>
<td>$\Phi 1&quot; \times 2 \text{ mm}$</td>
<td>$\Phi 1&quot; \times 1 \text{ mm}$</td>
<td>$\Phi 1&quot; \times 1 \text{ mm}$</td>
</tr>
<tr>
<td>Distance between substrate and target</td>
<td>6 cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sputtering power</td>
<td>20 W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar gas pressure</td>
<td>1 Pa (6.0 sccm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deposition time</td>
<td>20 min</td>
<td>30 min</td>
<td>30 min</td>
</tr>
<tr>
<td>Thickness</td>
<td>150 nm</td>
<td>500 nm</td>
<td>500 nm</td>
</tr>
</tbody>
</table>

Figure 2 shows a side view of the magnetron sputtering deposition system. Two magnetron sputtering cathodes were installed from the upper flange of a vacuum chamber. The deposition parameters were listed on Table 1. The 1 inch tantalum, copper, or platinum was attached on one of the sputtering cathode, and sputtering power of 20 W was applied from a DC power supply. Another sputtering cathode was prepared for producing multi-layer films. A 5 min pre-sputtering was performed before deposition. Single crystalline Si(100) substrates were used as the substrates. Argon gas was introduced to the vacuum chamber at a flow rate of 6.0 sccm to obtain the vacuum pressure of 1 Pa during the deposition. The thicknesses of the films were monitored using a quartz film thickness monitor.

RESULTS AND DISCUSSION

Figure 3 shows acceleration voltage dependences of the sputtering depths of tantalum irradiated with ethanol cluster ion beams with the dose of $1 \times 10^{15}$ ions/cm$^2$. The red circles indicate the sputtering depths of tantalum kept in vacuum after the deposition. The black squares indicate the sputtering depths of tantalum exposed to the air after deposition. The both sputtered depths increased with the acceleration voltage of the ethanol cluster ion beam, and showed no saturation within the acceleration voltage range from 3 to 9 kV.

Figure 4 shows dose dependences of the sputtering depths of tantalum irradiated with ethanol cluster ion beams with the acceleration voltage of 9 kV. As Fig. 3, the red circles indicate the sputtering depths of tantalum kept in vacuum after deposition, and the black squares indicate those exposed to the air after deposition. The sputtered depths of the tantalum irradiated by the ethanol cluster ion beam increased with the acceleration voltage of the ethanol cluster ion beam, and showed no saturation. Thus, it can be possible to realize deeper etching by increasing the dose of the ethanol cluster ion beam.

Figure 3: Acceleration voltage dependences of sputtered depths of tantalum irradiated with ethanol cluster ion beams.

Figure 4: Dose dependences of sputtered depths of tantalum irradiated with ethanol cluster ion beams.
Figure 5: Sputtering yields of tantalum, copper, and platinum induced by ethanol cluster ion beams.

Figure 5 shows the sputtering yields of tantalum, copper, and platinum induced by the ethanol cluster ion beam irradiation at the acceleration voltage of 9 kV. As Figs. 3 and 4, the red circles indicate the sputtering yields of tantalum, copper, and platinum kept in vacuum after the deposition, and the black squares indicate those exposed to the air after the deposition. The sputtering yields of tantalum, copper, and platinum irradiated with an argon monomer ion beam at 500 eV were also plotted as blue triangles [10]. The sputtering yields of tantalum, copper, and platinum irradiated by ethanol cluster ion beam were 87, 26, and 46 times higher than those irradiated by argon monomer ion beam at 500 eV, respectively. The sputtering yields of tantalum, copper, and platinum kept in vacuum were also 3.2, 2.9, and 3.5 times higher than those exposed to the air after deposition, respectively. These differences in the sputtering yields are possibly due to the influence of oxygen and moisture to the active surface of metal films just after deposition to form passive layer. Therefore, the possibility of an effective liquid cluster ion beam processing on metal films has been demonstrated.

SUMMARY

We examined the possibility of liquid cluster ion beam processing of metal films by irradiating ethanol cluster ion beams on tantalum, copper and platinum films. The sputtering yields of tantalum, copper, and platinum irradiated with ethanol cluster ion beam were 87, 26, and 46 times higher than those irradiated with argon monomer ion beam at 500 eV, respectively. Thus, it can be said that the possibility of the liquid cluster ion beam processing of metal films has been demonstrated.

REFERENCES