A High-Contrast Inorganic Ion Resist Using Amorphous WO₃ and MoO₃

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Ion-beam modification of amorphous W03 and Mo03 films has been studied to obtain a high-resolution inorganic ion resist. The films irradiated by a beam of singly-charged sodium ions with an accelerating voltage of 4-15 kV exhibit a resistive property of extremely high contrast ($\gamma \approx 8$ -10) at ion doses beyond a threshold value D_{th}. The voltage dependence of D_{th} suggests that the resistive property is a result of the insulator-metal transition of tungsten and molybdenum bronzes formed by ion implantation. This is also supported by measurements of optical and electrical properties of the irradiated films.

§1. Introduction

Ion-beam modification of materials is potentially useful for microfabrication of semiconductors. To obtain high resist sensitivity and resolution by combining the merits of ion beams and inorganic resists, we have studied the effect of ion-beam irradiation on thin amorphous films of transition metal trioxides, WO_3 and MOO_3 . These films are known to show electrochromic coloration by ion injection and to be applicable to passive display devices.¹⁾ This phenomenon is related to the formation of tungsten or molybdenum bronzes, M_XO_3 or M_XOO_3 (0<x≤1): M=H, alkaline metals, alkali earth metals, rare earth elements, Ag, In, Sn, etc.

In a previous paper,²⁾ we reported properties of WO₂ films as a negative-type ion resist with extremely high contrast. The films irradiated by a beam of sodium ions with relatively low energies become abruptly insoluble in alkaline solution at a threshold dose. The optical absorption spectra of the irradiated films suggested the formation of sodium tungsten bronze Na_xW0_3 by ion implantation. The resistive property was therefore taken to indicate the metal transition of the target surface at the threshold dose. This paper is a detailed report of the effect of ion irradiation on WO3 and MoO3 films, with some new experimental results of the change in their optical and electrical properties.

§2. Experimental

Thin films of WO_3 and MOO_3 were deposited onto In_2O_3 coated glass substrates by resistance-heated evaporation. The substrate temperature was about 150°C and the as-evaporated films were in the amorphous state. The film thickness was between 40-880 nm. The as-evaporated films appeared to be pale blue in transmission.

The ion source used in this experiment was a thermionic emitter consisting of a Pt filament and sodium silicate. In this type of emitter, both impurity ion emission and neutral-atom desorption are negligible after preliminary operation for several hours.^{3,4)} The film was irradiated by a beam of singly-charged sodium ions with a diameter of about 1 mm and a current density of 1-5 μ A/cm². The beam was scanned appropriately. The accelerating voltage of the ions was 4-15 kV, and the ion dose was controlled by the irradiation time. The secondary electrons from the target were collected by a hemispherical electrode with a hole in it to admit the ion beam.

Development after the irradiation was done by chemical etching in an aqueous solution of NaOH (0.01-0.04 N). The etching rate of the as-evaporated films in the 0.01 N solution was about 100 nm/min. Development was continued until the nonirradiated parts of the film were completely removed. The exposure characteristics were measured from the solubility of the films irradiated under various accelerating voltages and doses. The optical absorption spectra of the films before and after the irradiation, together with their change after electrolytic bleaching, were also measured separately. The electrical properties were measured from the change in the sheet resistance of the irradiated films with ion dose. This measurement was done by the four-probe method.

§3. Results and Discussion

In the low-dose region, the irradiated films were easily etched off in the same way as as-evaporated ones. However, they exhibited an abrupt change in solubility at a certain threshold dose. The contrast curves of WO_3 and MOO_3 films are shown in Fig. 1; the normalized film thickness remaining after the exposure and the subsequent development are plotted as a function of ion dose for various accelerating voltages. The initial film thickness is shown in the figure. The films showed no signs of sputtering.

The contrast value γ determined from the curves in Fig. 1 reaches 8-10, which is considerably higher than that of conventional, organic, negativetype ion resists.⁵⁾ This high contrast is characteristic of inorganic resists.⁶⁾ It appears that the distinction is based primarily on intrinsic differences in the mechanism of the excitation of the film. In conventional organic resists, it is very difficult to obtain high contrast because of the existence of various relaxation processes of excited states.



Fig. 1. Contrast curves of WO_3 and MOO_3 films with respective thickness of 100 and 200 nm exposed to ions with different accelerating voltages.



Fig. 2. Threshold dose for some WO_3 films as a function of accelerating voltage of ions. The voltage dependences of the doses required to obtain a sodium composition at the surface of 0.2 and 0.3 are also shown by dashed lines.

The threshold dose D_{th} of some WO₃ films, defined as the dose which results in 50% thickness remaining, is shown by solid lines in Fig. 2 as a function of the accelerating voltage V. The D_{th} value, which is almost independent of the film thickness, increases gradually with increasing V, i.e., the sensitivity somewhat decreases with V. The sensitivity to ion irradiation depends more weakly on V and film thickness than does the sensitivity to electron irradiation.⁷⁾ This is reasonable, since ion irradiation with voltages of about 10 kV produces a substantial surface effect, not a volume effect. For MoO₃ films, D_{th} behaved in a way similar to WO₃ films.

According to the calculation based on the LSS theory, the projected range R_p of Na⁺ for accelerating voltages of about 10 $kV^{\breve{}}$ in WO_3 and MoO_3 films shows the voltage dependence similar to the above D_{th} vs. V curves, as shown in Fig. 3. The similarity between these two dependences suggests that the change in sensitivity with V is related to the change in the sodium concentration near the surface. A possible explanation of the ion-beam modification observed is thus the formation of sodium tungsten or molybdenum bronzes, Na_xWO3 or Na Moo, by ion implantation. These bronzes are known to show the insulator-metal transition at an x value of about 0.2-0.3.8,9) The resistive



Fig. 3. Projected range of sodium ions in amorphous $\rm WO_3$ and $\rm MoO_3$ films as a function of accelerating voltage.

property of the irradiated films can thus be explained from the change in the chemical potential associated with the metal transition at the threshold dose.

Dashed lines in Fig. 2 show the voltage dependences of $D_{0.2}$ and $D_{0.3}$ which are the doses required to obtain a sodium composition at the surface of x=0.2 and 0.3, respectively. The calculation was based on the LSS theory, and it was assumed that the Na⁺ distribution profile is Gaussian and ions theoretically predicted to lie outside the surface simply accumulate at the surface. The behavior of $D_{0.2}$ and $D_{0.3}$ agrees very well with that of D_{th} . This confirms the hypothesis mentioned above. Similar results have also been obtained from MoO₃ films.

After ion irradiation, the films acquired a blue coloration and took on a metallic luster at high doses. The optical absorption spectra of WO3 film before and after ion irradiation are shown in Fig. 4 by solid lines. As-evaporated films have a pale-blue appearance possibly because of the formation of $H_{x}WO_{3}$ during the evaporation. After irradiation with a sufficient dose beyond D_{th} , the characteristic absorption of tungsten bronze increases. The spectrum after irradiation is similar to that obtained from Na_vWO_3 produced electrolytically. 10) In addition, the as-evaporated film was easily bleached electrolytically, whereas the irradiated one was not, as shown in Fig. 4 by dashed lines. These distinct properties are presumably due to a great difference in

the diffusion constant of H⁺and Na⁺.

Further support for the above explanation is provided by the behavior of the sheet resistance R_s of the films during irradiation. Figure 5 shows the change in R_s of two MoO₃ films with ion dose. As the dose approaches D_{th}, R_s is rapidly decreased by about three orders of magnitude. The R_s value of as-evaporated MoO₃ films was about $10^9 \Omega/\Box$. The change in conductivity of the implanted layer from the initial value extends over



Fig. 4. Optical absorption spectra of $W_{0,3}$ film before and after ion irradiation. The curves after electrolytic bleaching are also shown by dashed lines.



Fig. 5. Sheet resistance of MoO_3 films as a function of ion dose. The threshold dose is also shown by the arrow.

several orders of magnitude, since the projected range of Na⁺ at V=12 kV comprises only 1.4-8.3% of the total film thickness. This result is consistent with the metal transition of Na Moo, at the threshold dose.

Another possible effect of the ion irradiation is some structural change of the film as a result of energy deposition or some compositional change of the surface layer. More detailed surface analysis is required in order to verify the formation of tungsten or molybdenum bronzes.

§4. Summary

Thin amorphous films of WO_3 and MoO_3 exhibit resistive properties when irradiated with relatively low-energy ions. A significant change in solubility of the irradiated films in alkaline solutions was observed at a certain threshold dose with accelerating voltages of 4-15 kV. These films are potentially useful as a negative-type inorganic ion resist with extremely high contrast.

The voltage dependence of the sensitivity suggests that the resistive property is a result of the formation of tungsten or molybdenum bronzes and the subsequent metal transition at the thresh-This was also supported by the optical old dose. and electrical properties of the ion-irradiated films. Ion-beam modification of amorphous WO2 and MoO3 may not only be applicable to microfabrication, but also metallization techniques. In practice, the ion beam of H leading to production

of $H_{x}W_{3}$ and $H_{x}M_{3}O_{3}$ is preferable for this study. Systematic investigations of the resistive properties of WO3 and MoO3 films, including the surface analysis, the resolution performance, and the applicability to dry etching process, are also in progress.

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