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Copper nitride thin films prepared by radio-frequency reactive sputtering

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Copper nitride thin films were obtained by the reactive sputtering method. A metallic copper target was sputtered in nitrogen gas with radio-frequency (rf) magnetron sputtering equipment. Highly [100]-oriented polycrystalline films of the cubic anti-ReO₃ structure were obtained. Films with a lattice constant above 3.868 Å were conductors, while films with a lattice constant below 3.868 Å were insulators. The resistivity of conducting films was $0.5\text{--}3 \times 10^{-2} \Omega \text{ cm}$. The insulating films showed an optical energy gap of 1.3 eV, while the conducting films showed a smaller value which decreased with decreasing resistivity. © 1995 American Institute of Physics.

I. INTRODUCTION

Copper nitride (Cu₃N) has the cubic anti-ReO₃ structure. Since Cu atoms do not occupy the close-packing site of the (111) plane, insertion of Cu or another atom into the body center of the anti-ReO₃ structure is possible. That is, Cu₃N has the possibility (in applications) to be an inorganic host material like WO₃, which makes conductive tungsten bronzes by inserting some metal atoms into the ReO₃ structure. However, all the Cu₃N films reported¹⁻⁴ have been insulators. In addition, Cu₃N is stable at room temperature, while the thermal decomposition takes place at about 350–450 °C. Previous studies have been mainly concerned about the applications of its low decomposition temperature. Asano *et al.*¹ prepared the films by ion-assisted vapor deposition, and made preliminary experiments of the write-once optical recording on this film using the heat mode. Maya² obtained the films by dc sputtering, and explored the feasibility of using the coatings to generate microscopic metal lines by maskless laser writing.³

Our objective is to prepare copper nitride thin films by using reactive rf magnetron sputtering of a copper target. The sputtering parameters used were substrate temperature, rf power, and total pressure. The electrical and optical characteristics are clarified, and the effects of deposition conditions on the measured structure of the film are discussed.

II. EXPERIMENT

In preparing copper nitride films, rf (13.5 MHz) magnetron sputtering equipment (Osaka Vacuum Co. Ltd.)^{5,6} was used with a 99.99% pure copper target of 10 cm in diameter and 1 mm thick. The rf power was 20–400 W, the sputtering gas was 99.999% pure nitrogen, and its flow rate ranged 10–200 sccm. The separation distance between the substrate and the target was 48 mm. The chamber vacuum just before growth was less than 2.0×10^{-6} Torr. The substrate was heated by a lamp heater to a temperature in the range 50–300 °C. It was measured using a chromel–alumel thermocouple attached to the front of the substrate holder. During the run at a substrate temperature below 200 °C, the temperature increased because of the effect of plasma heating. Since

the rate decreased with increasing time, the final substrate temperature was used as a representative substrate temperature. The total sputtering pressure ranged from 0.76 to 28 mTorr. A 76×26 mm² borosilicate glass plate was used as the substrate.

The crystallinity of the film was analyzed by the x-ray diffraction (XRD) method (Shimadzu XD 610) with Cu K α radiation. The electric resistivity of the film was measured by the van der Pauw method. The carrier concentration and Hall mobility were measured by using the Hall effect. The optical transmittance of the film was obtained by means of a multi-purpose recording spectrophotometer. A blank glass substrate was inserted into the reference beam path of the spectrophotometer.

III. RESULTS AND DISCUSSION

Smooth copper nitride films were formed, which were transparent and colored dark brown on the glass substrate. Figure 1 shows the deposition rate as a function of rf power.

FIG. 1. Deposition rate as a function of rf power and total pressure.

FIG. 2. X-ray diffraction pattern of 133-nm-thick film on a borosilicate glass substrate.

and total pressure. A similar dependence on total pressure was observed in depositing InN and SnN_x films.^{5,6} Visual observations of the deposition at high total pressure showed that the surface of the target was covered with a black nitrated layer after each run.

Figure 2 shows a typical example of the x-ray diffraction pattern of the film on a glass substrate. The precise (100) and (200) peaks indicate that the film is composed of polycrystallites with a cubic anti- ReO_3 structure. A large peak of (100) indicates that the film is highly [100]-oriented. All samples showed similar x-ray diffraction patterns, indicating the highly [100]-oriented cubic anti- ReO_3 structure. The crystallinity strongly depends on deposition conditions. Below, the dependence is discussed by using the full width at half-maximum (FWHM) and integrated intensity of the diffraction peak corresponding to a (100) reflection.

Figures 3–5 show the FWHM and integrated intensity as functions of substrate temperature, total pressure, and rf power. The films were prepared by keeping two of the following three parameters constant: total pressure of 4.5 mTorr, rf power of 50 W, and a substrate temperature in a range of 50–140 °C which was the lowest substrate temperature under the effect of plasma heating. Comparisons of integrated intensity were made between films of nearly equal value of the thickness of film. Figure 3 shows that the integrated intensity increases with increasing substrate tempera-

FIG. 3. FWHM and integrated intensity as a function of substrate temperature. Films were prepared at constant total pressure (4.5 mTorr) and constant rf power (50 W). Film thickness is in the range 88–133 nm.

FIG. 4. FWHM and integrated intensity as a function of total pressure. Films were prepared at constant rf power (50 W) and substrate temperature in a range of 50–140 °C. Film thickness is in the range 78–97 nm.

ture, because of an enhanced surface diffusion of the adatoms at higher substrate temperatures.⁶ At substrate temperatures above 220 °C, however, the integrated intensities show very small values. In addition, the film was amorphous at 300 °C. These are attributable to lattice defects caused by surface adatom reemissions: i.e., the reevaporation of atomic nitrogen from the substrate at higher substrate temperatures.^{5,6} Figure 5 shows that the films of inferior crystallinity are prepared at higher rf powers, where the deposition rates show larger values.

For the electrical characteristics, not all the films were insulators, and some films of inferior crystallinity were conductors. For example, some films prepared at substrate temperatures below 100 °C were conductors, although the films prepared at substrate temperatures above 160 °C were invariably insulators. In fact, Fig. 3 shows that the films have inferior crystallinities at substrate temperatures below 100 °C. Figure 6 shows the insulator–conductor boundary of deposition conditions for the films prepared at substrate temperatures below 100 °C. A comparison of Fig. 6 with Figs. 4

FIG. 5. FWHM and integrated intensity as a function of rf power. Films were prepared at constant total pressure (4.5 mTorr) and substrate temperature in a range of 50–140 °C. Film thickness is in the range 97–147 nm.

FIG. 6. Insulator-conductor boundary of deposition conditions for films prepared at substrate temperatures below 100 °C.

FIG. 8. Lattice constant as a function of substrate temperature.

and 5 shows that the conditions for obtaining conducting films correspond to those for the films of inferior crystallinity.

Figure 7 shows examples of the absorption coefficients as a function of photon energy. The optical energy gap E_g for indirect transitions is obtained by extrapolating the full line to the abscissa. The value of E_g for the insulator is 1.3 eV, while the conductor shows a smaller value which decreases with decreasing resistivity.

The electric conductivity is inferred to be due to an insertion of Cu atoms into the body center of the anti- ReO_3 structure, like WO_3 , which makes conductive tungsten bronzes by inserting some metal atoms into the ReO_3 structure. That is, the inserted Cu atoms becomes a donor which releases a free electron as a carrier. Therefore, it is inferred that the difference between insulator and conductor is reflected by the differences in lattice constant for inserting Cu atoms.

Figures 8–10 show the lattice constant as functions of substrate temperature, total pressure, and rf power. The results in Fig. 8 were obtained at an rf power of 50 W, the results in Figs. 9 and 10 at a substrate temperature in a range of 50–100 °C, and the results in Fig. 10 at a total pressure of

4.5 mTorr. They are larger than that for powder (3.815 Å). The lattice constant increases with decreasing substrate temperature, decreasing total pressure, and increasing rf power. These conditions correspond to those for obtaining the films of inferior crystallinity, and consequently to those for obtaining the conducting films. Furthermore, the latter conditions can be expressed by using the critical value of a lattice constant. That is, the films with a lattice constant above 3.868 Å are conductors, while the films with a lattice constant below 3.868 Å are insulators.

Figure 11 shows the resistivity, Hall mobility, and carrier concentration for the conducting films. The results obtained at various deposition conditions are correlated as a function of lattice constant. The resistivity is $0.5\text{--}3 \times 10^{-2} \Omega \text{ cm}$. The carrier concentration does not increase with increasing lattice constant. This fact suggests that the increase in lattice constant is not due to the increase in carrier concentration, i.e., the insertion of Cu atoms. That is, the film with a lattice constant above the critical value 3.868 Å enables the insertion of a certain number of Cu atoms. The number of atoms is irrelevant to the increase of lattice constant.

FIG. 7. Relation between absorption coefficient and energy of incident photons.

FIG. 9. Lattice constant as a function of total pressure.

FIG. 10. Lattice constant as a function of rf power.

FIG. 11. Resistivity, Hall mobility, and carrier concentration as a function of lattice constant.

IV. CONCLUSIONS

Copper nitride thin films were obtained by the reactive sputtering method. The metallic copper target was sputtered in nitrogen gas with rf magnetron sputtering equipment. Highly [100]-oriented polycrystalline films of the cubic anti-ReO₃ structure were obtained. Films with a lattice constant above 3.868 Å were conductors, while films with a lattice constant below 3.868 Å were insulators. The resistivity of conducting films was $0.5\text{--}3 \times 10^{-2} \Omega \text{ cm}$. Insulating films showed an optical energy gap of 1.3 eV, while conducting films showed a smaller value which decreases with decreasing resistivity.

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