CHEMISTRY LETTERS, pp.599-602, 1974. Published by the Chemical Society of Japan

CRYSTAL STRUCTURE OF REACTIVE SPUTTERED SILVER FILMS AND THERMAL DESORPTION OF OXYGEN FROM THESE FILMS

Sadao TANAKA, Tetsuya ABE, and Toshiro YAMASHINA
Department of Nuclear Engineering,
Hokkaido University, Sapporo 060

The crystal structure and resistivity of silver films sputtered in an oxygen atmosphere and the thermal desorption of oxygen from these films were studied. The sputtered silver films prepared under the oxygen of 1.5 x 10^{-4} and 3 x 10^{-4} Torr contained very fine fcc silver crystals and Ag_2O crystals. The thermal desorption showed that all the reactive sputtered silver films contained a considerable amount of an amorphous phase.

Recently, there has been a great interest in reactive sputtering method of preparing thin films in the microelectronics industry.1),2) We gave attention to the advantage of sputtered films that their reactivity can be adjusted by controlling atmosphere on sputtering (oxygen, nitrogen, hydrogen, etc.). Thus we will apply these sputtered films to the catalytic study. Silver is unique among metal catalysts in its exceptional ability to catalyze the ethylene epoxidation.3-6) Accordingly the crystal structure of silver films prepared by this method and the thermal desorption of oxygen from these films were studied in the first place.

Various sputtering conditions were examined with nominal oxygen percentages from 0 to 15% in argon and total pressure (P_{O_2} + P_{Ar}) 5 x 10^{-3} Torr. The sputtered films were approximately 7500 Å in thickness. The variation of the film resistivity with the oxygen pressure during sputtering was studied. As oxygen pressure increased from 0 to 3 x 10^{-4} Torr, the resistivity of the film remained unchanged. However, a remarkably large increase of the resistivity was observed above 6 x 10^{-4} Torr, as shown in Fig. 1. The thermal desorption of oxygen from these films was also examined. The raising rate of temperature was 1°/6 min. The removable gases were evacuated by heating the silver films while the pressure in the system was recorded. The desorbed gases (O_2, CO_2, H_2O, CO, HCHO, etc.) were simultaneously analyzed by a quadrupole mass spectrometer. It was found that many different binding states of oxygen (O_I - O_V) existed on or in all the silver films, as shown in Fig. 2. The peaks of oxygen O_I - O_V were observed at 70°, 110°, 125°, 280°, and 300°C, respectively. A very small amount of O_I, O_{II}, O_{III}, and O_V was observed, while a very large amount of O_{IV} was observed and the amount of O_{IV} was strongly dependent on the oxygen pressure during sputtering. When ethylene was introduced over these films at 150°C, the oxidation of ethylene proceeded easily to produce CO_2, H_2O, and C_2H_4O. The reaction rate between gaseous ethylene and oxygen contained in all the reactive sputtered films was two-order faster than that between gaseous ethylene and adsorbed oxygen on the sputtered pure silver film at 200°C. The oxygen was completely removed from these films at 150°C by reduction with ethylene and the amount of oxygen in these films was roughly estimated by consumed amount of ethylene. These results were shown in Table 1. The amount of oxygen was found to increase with the oxygen pressure during sputtering.

The crystal structure of these sputtered films was determined by X-ray diffraction. The X-ray diffractometer trace of the sputtered silver film prepared in pure argon was given in Fig. 3(a). All the observed reflection peaks could be attributed to the fcc phase of silver crystal. Accordingly, it was concluded that the sputtered pure silver film consisted of very fine fcc silver crystals and these crystals were oriented at random likewise silver crystal powders. The observed reflections of the reactive sputtered films prepared under the oxygen of 1.5×10^{-4}, 3×10^{-4} and 7.5×10^{-4} Torr were shown in Fig. 3(b), (c), and (d), respectively. It was shown from the X-ray diffraction pattern that the silver films ($Po_2 = 1.5 \times 10^{-4}$ and 3×10^{-4} Torr) contained very fine fcc silver crystals and a very small amount of Ag_2O crystals. The removable oxygen (O_I, O_{II}, O_{III}, and O_{IV}) could be eliminated by evacuation for 20 hr at 270°C, being confirmed by a measurement of the amount of redesorption and ethylene consumption. However, the X-ray diffraction patterns and their intensities were not changed by the evacuation at 270°C. It was considered that the oxygen was removed from an amorphous phase and these two sputtered films contained the amorphous phase in abundance. In succession, these films were evacuated at 350°C for 20 hr. The reflection at 32.7° of Ag_2O crystals disappeared and only the reflections of fcc silver crystals were observed. It was found that their intensities of all silver crystal reflection peaks increased about twice by heating for a week. So it was considered that the oxygen O_V of these silver films was that of Ag_2O crystals. The X-ray diffraction trace of the film ($Po_2 = 7.5 \times 10^{-4}$ Torr) was remarkably different from the trace of those films ($Po_2 = 1.5 \times 10^{-4}$ and 3×10^{-4} Torr). Only the two reflections at 65° and 30.5° corresponded with the reflections of fcc silver crystals and Ag_2O crystals, respectively. The other broad reflections at 37.7° and 81.1° were not explainable. The halfwidth of these two reflection peaks were three times larger than those of normal fcc silver reflection peaks. Removable oxygen species (O_I, O_{II}, and O_{III}) were evacuated from this film at 170°C for 20 hr. Then the small reflection peaks of fcc silver crystals increased. Successively, this film was evacuated at 270°C for 20 hr and the oxygen (O_{IV}) was removed. However, the broad reflections at 37.7° and 81.1° were still observed. Consequently these oxygen species (O_I, O_{II}, O_{III}, and O_{IV}) were considered to be removed from the amorphous phase of the reactive sputtered film. The X-ray diffraction pattern of this film was strikingly changed by the evacuation at 350°C for 20 hr. The broad reflections and the reflection of Ag_2O crystals disappeared completely and sharp reflection peaks of fcc silver crystals appeared likewise sputtered pure silver film. So it was considered that the oxygen O_V of this film was that of Ag_2O crystals likewise the films ($Po_2 = 1.5 \times 10^{-4}$ and 3×10^{-4} Torr). The broad reflections would be due to a some imperfect phase of silver and this imperfect phase would be changed to the perfect fcc silver crystals by heat treatment at 350°C.

REFERENCES

1) W.D.Westwood and N.Waterhouse, J.Appl.Phys., 42, 2946 (1971).
2) K.Tanaka, A.Kunioka, and Y.Sakai, Japanese J.Appl.Phys., 8, 681 (1969).
3) H.H.Voge and C.R.Adams, Advances in Catalysis, 17, 151 (1967).
4) W.M.H.Sachtler, Catalysis Rev., 4, 27 (1970).
5) R.B.Clarkson and A.C.Cirillo, Jr., J.Vac.Sci. & Technol., 9, 1073 (1972).
6) G.Rovida, F.Protesi, M.Maglietta, and E.Ferroni, J.Vac.Sci. & Technol., 9, 769 (1972).

Table 1. The ratio of oxygen contained in the reactive sputtered silver films

	Oxygen pressure during sputtering	Ratio of oxygen to silver atom (atomic percent)
No.1	no oxygen	0 %
No.2	1.5×10^{-4} Torr	3 %
No.3	3.0×10^{-4} Torr	8.5%
No.4	7.5×10^{-4} Torr	30.5%

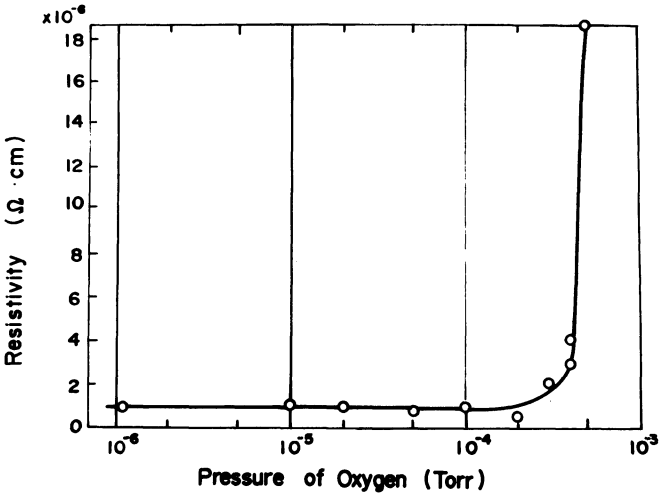

Fig. 1. Resistivity of the reactive sputtered films as a function of oxygen pressure during sputtering.

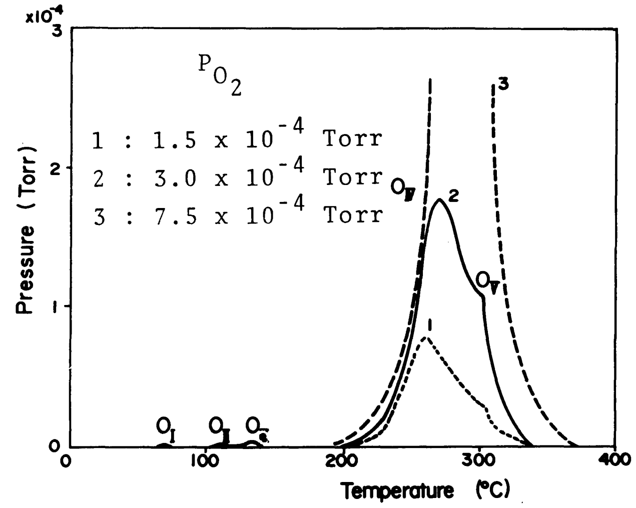

Fig. 2. Thermal desorption spectra of oxygen from the reactive sputtered films prepared at various oxygen pressures.

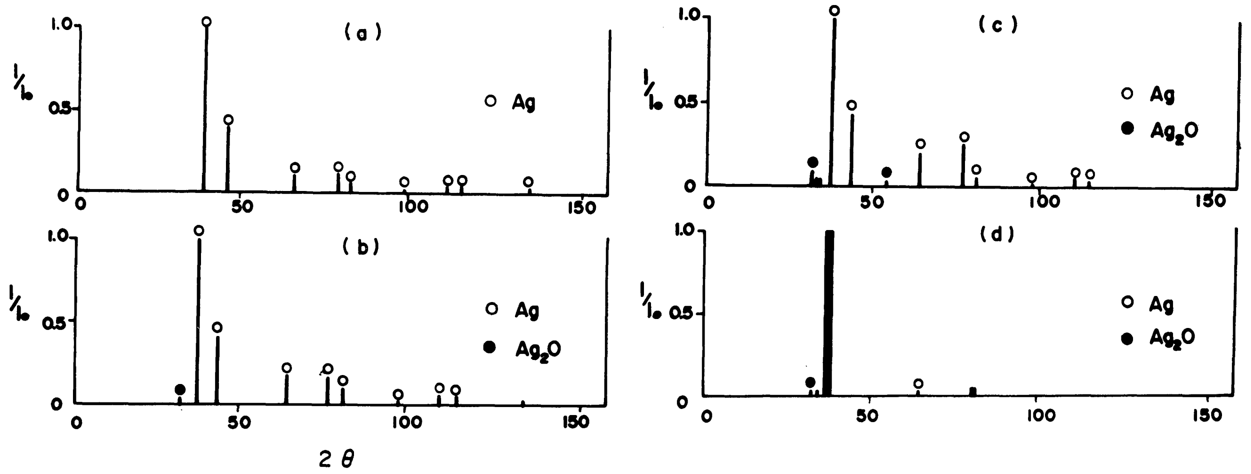

Fig. 3. X-ray diffraction patterns of reactive sputtered silver films prepared at various oxygen pressures.

(a) in pure argon

(b) $P_{O_2} = 1.5 \times 10^{-4}$ Torr

(c) $P_{O_2} = 3.0 \times 10^{-4}$ Torr

(d) $P_{O_2} = 7.5 \times 10^{-4}$ Torr

(Received January 25, 1974)