北見工業大学研究報告
第12巻 第1号 (昭和56年)

Memoirs of the Kitami Institute of Technology
Vol. 12 No. 1 (1981)

The Resistive and Structural Properties of Evaporated Chromium and Chromium-Copper Alloy Thin Films*

by Toshiji UMEZAWA** and Hideko YAHATA***

(Received April 30, 1980)

Abstract

The resistive and structural properties of chromium and chromium-copper alloy films were found to vary significantly with changes in substrate temperature and deposition rate, and with heat treatment.

Properties such as resistance, temperature coefficient of resistance, and Hall coefficient differ considerably from the corrected bulk values.

From an investigation of the structural properties of films, it was found that the lattice constants of the as-deposited chromium and copper films were somewhat smaller than the ASTM value.

Heat treatment in air at 200°C for 3 hrs has improved the resistive properties as determined on 500 Å thick films containing a copper content lower than 60 wt. %.

I. Introduction

The physical properties of vacuum deposited films depend primarily on the following factors: composition and impurity content of evaporant, source temperature, residual gas composition and pressure, deposition rate, and temperature, surface structure, binding forces and cleanliness of the substrate surface.[1),2),3),4)]

The present study is concerned with the three parameters of substrate temperature, deposition rate and heat treatment for evaporated chromium and chromium-copper alloy thin films. Since these films are of practical importance as resistor films and adhesion-increasing underlayers for other metal depositions, the evaporations were performed in a high vacuum of 1×10^{-5} torr. The films were deposited on the frosted soda glass at the temperature of 200 or 300°C and at a deposition rate ranging from 3 to 18 angrostrom per second from tungsten-strip boat.

Our study shows that consistent electric properties can be obtained if both the substrate temperature and deposition rate are closely controlled, and also shows that heat-treatment in air at 200 or 300°C changes the electrical properties of films, but is useful for the stabilization.

---

* A part of this paper was presented at the annual meeting of the institute of electronics and communication engineers of Japan.

** Department of Electronic Engineering, Kitami Institute of Technology.

*** The Faculty of Dental Surgery, Hokkaido University.

II. Experimental Details

The experimental technique employed in this study is specified by the following three predominant features.

1. The number of evaporation runs required for obtaining an experimental result of varied deposition condition has been minimized by considering the reproducibility of resistive properties for the films of four different thicknesses 200, 500, 800 and 1200 angstroms.
2. The deposition parameters of deposition rate, substrate temperature and evaporation time were closely controlled by exactly calibrated monitors in order to minimize the random parameter variation from run to run.
3. The physical state of the films was determined as closely as possible by measuring in a wide range of structural, electrical and thermal properties related to each film.

The next section will show how these features have been treated in practice.

(1) *Substrate Preparation*

In order to minimize the influence of the substrate on the films structural and resistive properties, commercial frosted soda glasses were used as substrate for the study of electrical properties and x-ray diffraction analysis, since this glass has a much smoother surface than other commercial soda glass. The substrates were cleaned by ultrasonical agitation in a warm detergent solution, and were rinsed in distilled water for 45 minutes (three rinsings of 15 minutes each). The water was removed by an isopropyl alcohol ultrasonic bath, and finally the glass was dried in isopropyl alcohol vapour. Copper micromeshes coated with carbon and collodion films were also used as substrates for the preparation of samples for electron transmission microscope and diffraction studies.

(2) *Evaporation Equipment*

The basic evaporator consisted of a 40 cm dia. steel chamber with a 6 inch oil diffusion pump. A vacuum of at least 1×10^{-5} torr was maintained during the evaporation through the aid of a liquid nitrogen cold trap. The substrate holder assembly and rotating mask holder were mounted on two separated steel discs, each holder containing 8 substrates and masks. These substrates were electrically heated and the temperature was measured by a chromel-constantan thermocouple connected to the surface thermometer. The evaporants were charged on two tungsten boats; one for resistive materials and the other for conductive electrode materials (mainly aluminum). The deposition rate and relative film thickness were controlled by a crystal oscillation type monitor, and the exact film thickness was determined by a multiple beam interferometry.

(3) *Film Evaluation*

The following film properties were measured: (a) film thickness, (b) electrical resistance, (c) temperature coefficient of resistance, (d) Hall coefficient, (e) crystallinity.

The electrical resistance was measured by a 6 figure digital LRC meter at 30 and 60°C, and a temperature coefficient of resistance (TCR) was determined from these values. The Hall coefficient measurement was performed in a 10 kilo-gauss magnetic field. The film structure and lattice constant determination for these films were made by transmission electron microscopy and diffraction, and x-ray diffraction. The compositions of Cr-Cu alloy films were determined by measuring the peak heights by electron micro probe analysis.

III. Results and Discussion

III-1. Electrical properties of Cr and Cr-Cu alloy thin films

III-1-1. Cr thin films

The correlation between electric resistive characteristics and substrate temperature during deposition of chromium films was evaluated under varied depo-

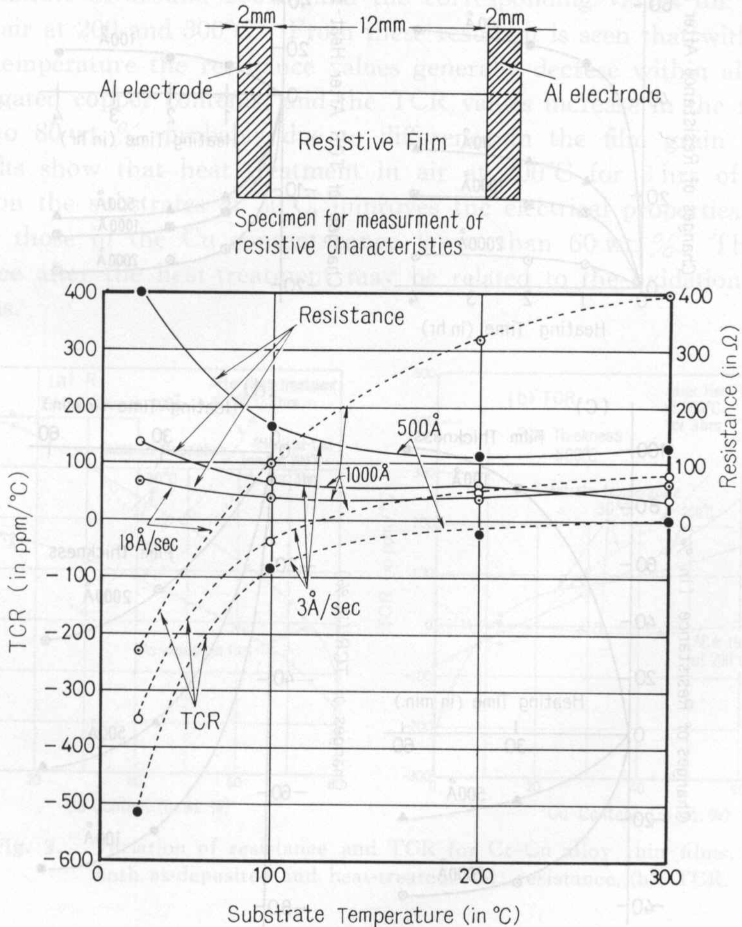


Fig. 1. Variation of resistance and TCR of evaporated chromium films under different deposition conditions.

sition rates and film thicknesses. These results were shown in Fig. 1. It was found that the films had a higher resistance as they were deposited on the substrates at lower temperature, and at a lower deposition rate. The TCR for the films generally varied from negative values to positive values with increased substrate temperature, and within the positive region they were greater as the deposition rate increased. It seemes that these features depend on the surface scattering and grain size effects in the films. These chromium films were heat-treated in air at 200 and 300°C, using an electric oven. Fig. 2 shows the influence of heat treatment on the resistance and TCR of films as a function of

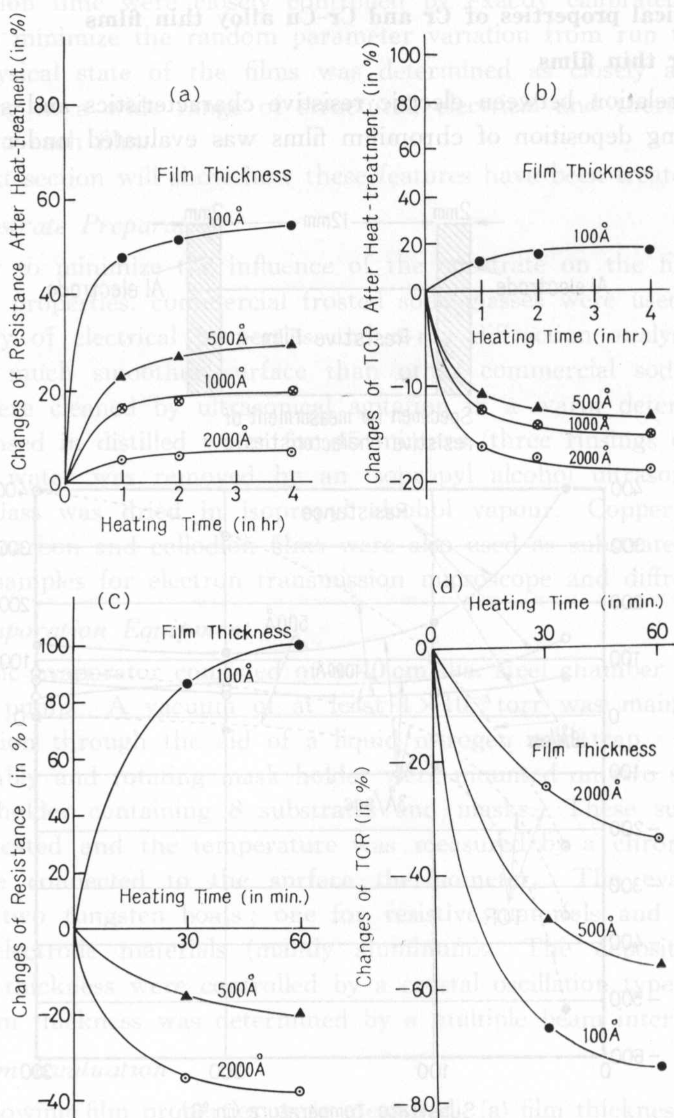


Fig. 2. Effects of heat-treatment on resistance and TCR of chromium films. (a) and (b); in air at 200°C, (c) and (d); in air at 300°C.

heating time. This figure also shows that heat-treatment at 200°C causes increases of resistance for films in all the investigated film thicknesses and decreases of TCR for films having thicknesses greater than 500 angstroms. Heat-treatment at 300°C causes a decrease in resistance for films having thicknesses greater than 500 angstroms and a decrease in TCR for all investigated film thickness ranges. This is probably due at 200°C to a decrease of effective thickness by thermal oxidation and at 300°C to a diminution of resistivity by the recrystallization of films having a thickness greater than 500 angstroms.

III-1-2. Cr–Cu alloy films

These films were prepared by vacuum evaporation from a tungsten boat charged with a powder mixture. The weight percentage of the films was determined by calculation using the peak heights of $CrK\alpha_1^3$ and $CuK\alpha_1^3$, obtained by x-ray micro-analysis for these films. Fig. 3 shows the resistance and TCR for the Cr–Cu alloy films as a function of Cu contents in the films deposited on the substrate at 30 and 200°C, and the corresponding values for films heat-treated in air at 200 and 300°C. From these results it is seen that with increased substrate temperature the resistance values generally decrese within all ranges of the investigated copper contents, and the TCR values increase in the range from 40 wt. % to 80 wt. %, probably due to difference in the film grain size. Also these results show that heat treatment in air at 200°C for 3 hrs of the films, deposited on the substrates at 30°C, improves the electrical properties, especially TCRs, for those in the Cu content range lower than 60 wt. %. The increase in resistance after the heat-treatment may be related to the oxidation of copper in the films.

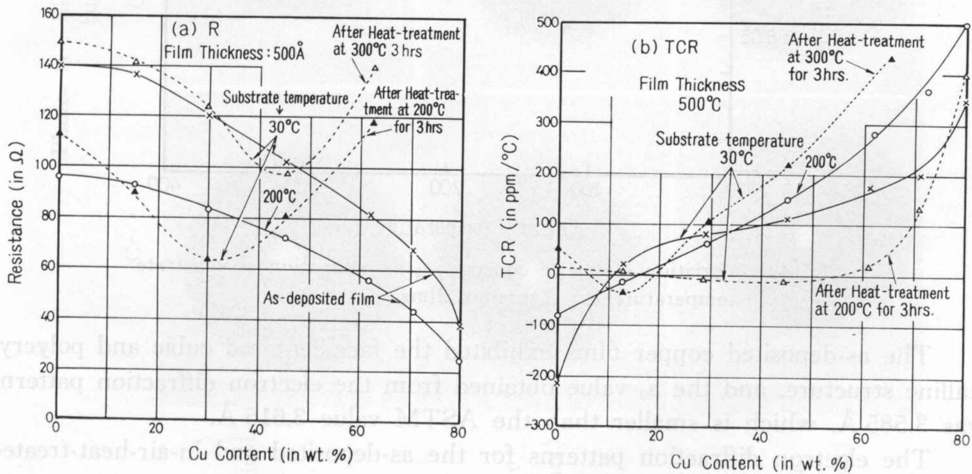


Fig. 3. Variation of resistance and TCR for Cr–Cu alloy thin films, both as-deposited and heat-treated. (a); resistance, (b); TCR.

III-2. Structural properties

Within the investigated substrate temperature and deposition rate range (25～300°C and 3～18 Å/sec, respectively), all chromium films exhibited the body-centered cubic structure. Over the entire substrate temperature range, the films about 200 Å thick deposited on the Cu micro-meshes coated with carbon and collodion films, as examined by electron diffraction, exhibited polycrystallin structure and were oriented at random. Films deposited on glass substrates exhibited slightly (110) orientation. From Debye-Scheller rings, the lattice constant a_0 value for chromium films deposited at room temperature was calculated to be 2.870 Å, and this a_0 value was significantly smaller than the ASTM value 2.8839 Å, as shown in Fig. 4, probably due to stronger stress in the films of about 200 Å thickness.

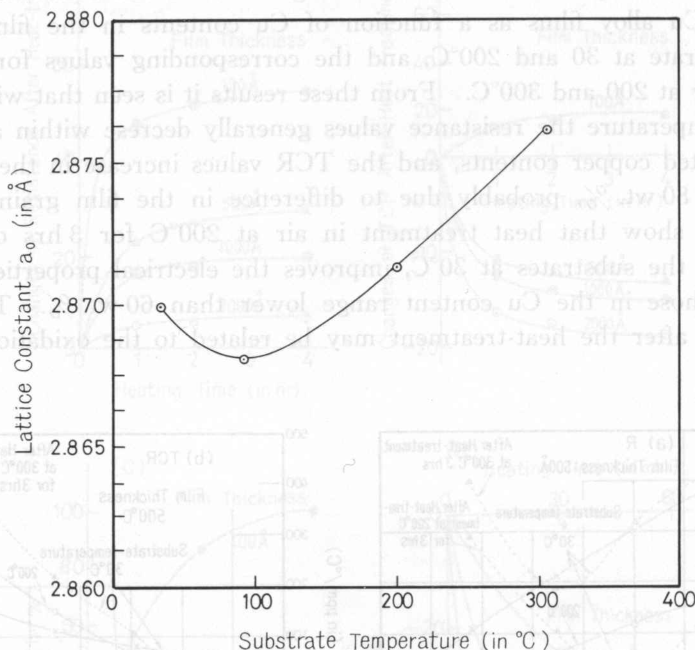
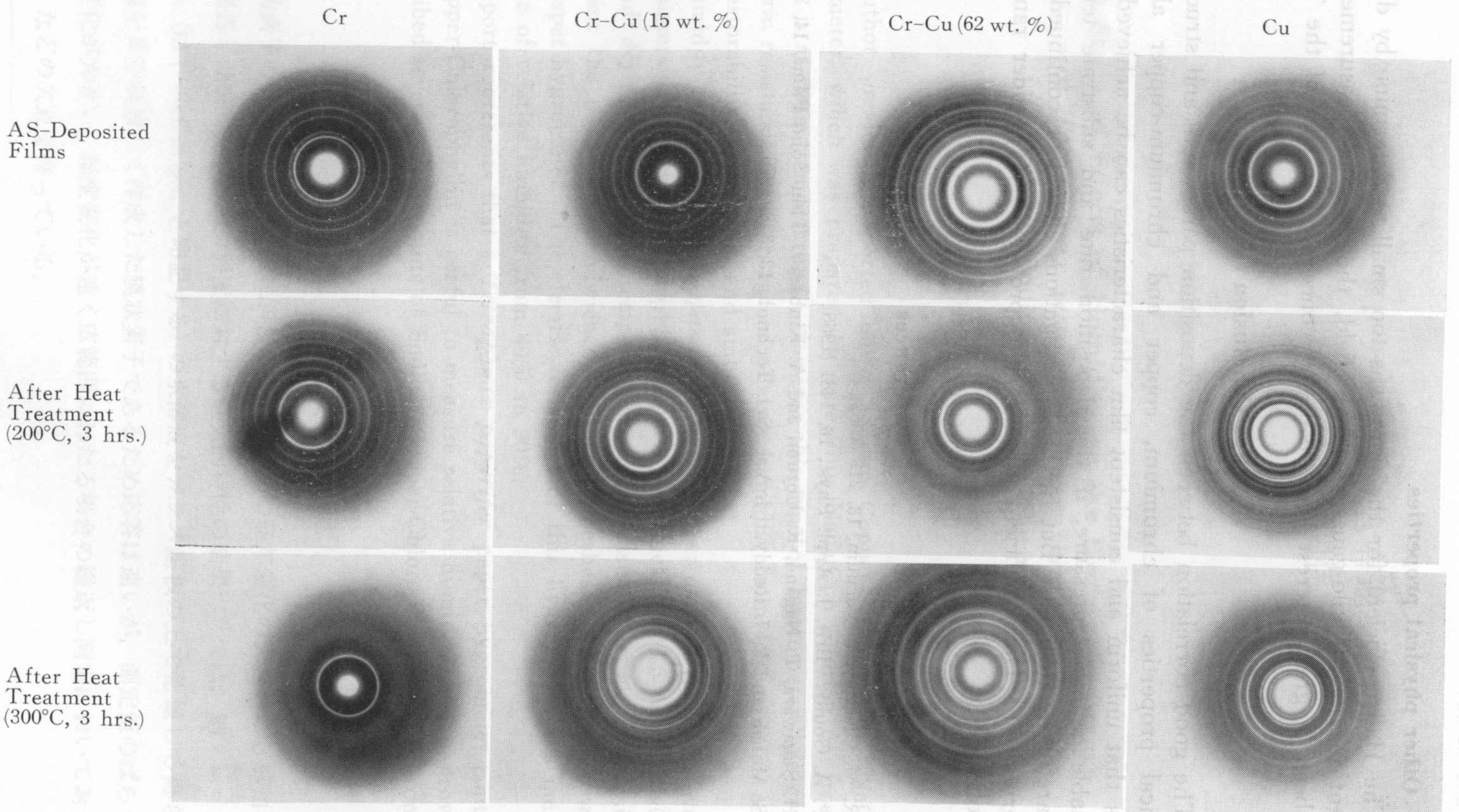


Fig. 4. Variation of lattice constant a_0 as a function of substrate temperature for chromium films.

The as-deposited copper films exhibited the face-centered cubic and polycrystalline structure, and the a_0 value obtained from the electron diffraction patterns was 3.585 Å, which is smaller than the ASTM value 3.615 Å.

The electron diffraction patterns for the as-deposited and in-air-heat-treated films of Cr, Cu and Cr-Cu alloy are shown in Photo. 1. These photographs show that the as-deposited Cr-Cu (62 wt. %) films exhibited rather an amorphous structure, and by the heat-treatment in air at 300°C, the copper in all Cr-Cu films was oxidized and exhibited CuO structure. These results for Cr-Cu alloy films are in agreement with the consideration of the results shown in Fig. 3.

Photo. 1. Electron diffraction patterns for Cr, Cr–Cu and Cu thin films, both as-deposited and heat-treated.



III-3. Other physical properties

The Hall coefficient for the films was too small to determine by d.c. measurement in the 10 kilo-gauss magnetic field, though this measurement would have been of great interest because it was concerned the sign of the TCR.

IV. Conclusion

The good correlation between the deposition parameters and structural and electrical properties of chromium, copper and chromium-copper alloy films shows that uniform and consistent film characteristics can be achieved at easily attainable chamber pressure, if the deposition rate and substrate temperature are carefully controlled. But further investigations should be continued, specially concerning the Hall coefficient and the film properties of a wider range of deposition rates.

References

1) R. M. Chapman: Vacuum, **13**, 213 (1963).
2) P. A. Gould: Brit. J. Appl. Phys., **16**, 1461 (1965).
3) H. Sugawara, T. Nagano, K. Uozumi and A. Kinbara: Thin Solid Films, **14**, 349 (1972).
4) S. Mohan and P. J. Reddy: J. Vac. Sci. Technol., **13**, 338 (1976).