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ANNEALING BEHAVIOUR, TCR VALUES AND DEFECT DENSITY FOR "COLD-CONDENSED" SILVER FILMS

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Key Words: Ag films, annealing behaviour, defect density

ABSTRACT

Thin silver films were deposited under vacuum of 10^{-6} Torr by thermal evaporation onto cooled glass substrates kept at low temperatures. Pure argon gas prevailed as residual gas. Annealing behaviour of the electrical resistance and defect density in Ag films was investigatd. Analysis of the result using Vand's theory showed that the variation of the function $F_\bullet$ expressing the law of distribution of the decay energies depends on the film thickness as well as on the deposition temperature. The evaluated activation energy was found to be about 0.1 and 0.2 eV for films deposited at 175 and 225 K respectively. For thickness $\leq$ 120 Å, the activation energy varied slightly with thickness for films deposited at 225 K. The temperature coefficient of resistance of a film of infinite thickness depended on the deposition temperature.

INTRODUCTION

It is a well-known fact that the resistivity of evaporated metal films is always higher than that of the bulk material. This is due to the fact that during the film growth process, a large number of lattice defects are incorporated. It was found that an irreversible decrease in the film resistance occurs if the film is heated beyond the deposition temperature (Flechon et al 1976, Renucci et al 1982, 1985). According to Vand's theory (Vand 1943), this decrease in the film resistance with temperature is attributed to specific defects or distortions such as lattice vacancies, interstatial atoms or combined vacancies and interstatials. These structural defects could be removed from the film by aging and/or anneaing.

Though evaporated silver films were studied extensively, the work on Ag films evaporated onto cold substrates is not comprehensive. Silver films deposited on cold substrates were found to display very strong surface enhanced Raman scattering (SERS) which was irreversibly lost when the films were heated (Pockrand et al 1981, Albano et al 1983, 1985 and Reed et al 1985). Schlemminger and Stark (1986) found that the resistivity of 200 Å thick Ag film decreased by annealing. Flechon et al (1976) applied Vand's theory on his data for Ag films which were prepared at 30° C by

chemical reduction in acquous solution. They found that the defect density decreased with increasing film thickness. To our knowledge, no work has been published on the defect density in Ag films evaporated onto cold substrates. The aim of this work is to investigate the effect of annealing on the electrical resistance of Ag films of different thicknesses (50 - 300 Å), and to study the dependence of the defect density on film thickness and deposition temperature.

EXPERIMENTAL DETAILS

Thin silver films (50 - 300 Å) were deposited at a constant condensation rate of 3 Å/s onto cooled glass substrates under vacuum of 10^{-6} Torr. Pure argon gas prevailed as residual gas in the vacuum system. Before film preparation, the substrates were cleaned and ion-bombarded by glow discharge. The substrate temperature was varied from 175 - 300 K in steps of 25 K. The temperature was measured using a calibrated chromel-alumel thermocouple fixed to the substrate surface. The condensation rate, as well as the film thickness,was determined using a quartz crystal thickness monitor. The films were held at the deposition temperature for 30 minutes prior to heating with a constant rate of 1 K/min from the deposition temperature to about 350 K. The change in the resistance was monitored, in situ, using a programmable digital multimeter (Keithley DMM 192). After a minimum in the film resistance was observed, the film was then subjected to cooling and heating cycles.

RESULTS AND DISCUSSION

1. Annealing Behaviour

The resistances of silver films of different thicknesses were studied as functions of temperature. The films were heated at a constant rate of 1K/min, that is subjected to "isochronal annealing". Figure 1 shows the variation of the resistance with temperature for films deposited at 175 K. The general behaviour obtained for films deposited at different temperatures in the range 175 - 300 K is the same as shown in Figure 1. The behaviour is characterized by an initial rapid drop in the resistance followed by a slow assymptotic decrease. This observed change in the resistance is irreversible, which is in agreement with reported results on the properties of silver and other materials in film form (Albano et al 1985, Renucci et al 1982, George and Joy 1980, Reda et al 1984, Schlemminger and Stark 1986). According to Vand's theory (Vand 1943), this decrease in the resistance is a result of the elimination of some defects in the film. Annealing leads to a better crytallographic structure and enhances surface flatness of the film and hence will cause a decrease in resistivity (Renucci et al 1982. Reda et al 1984, Lopez-Rios et al 1983, Wedler and Chandler 1980).

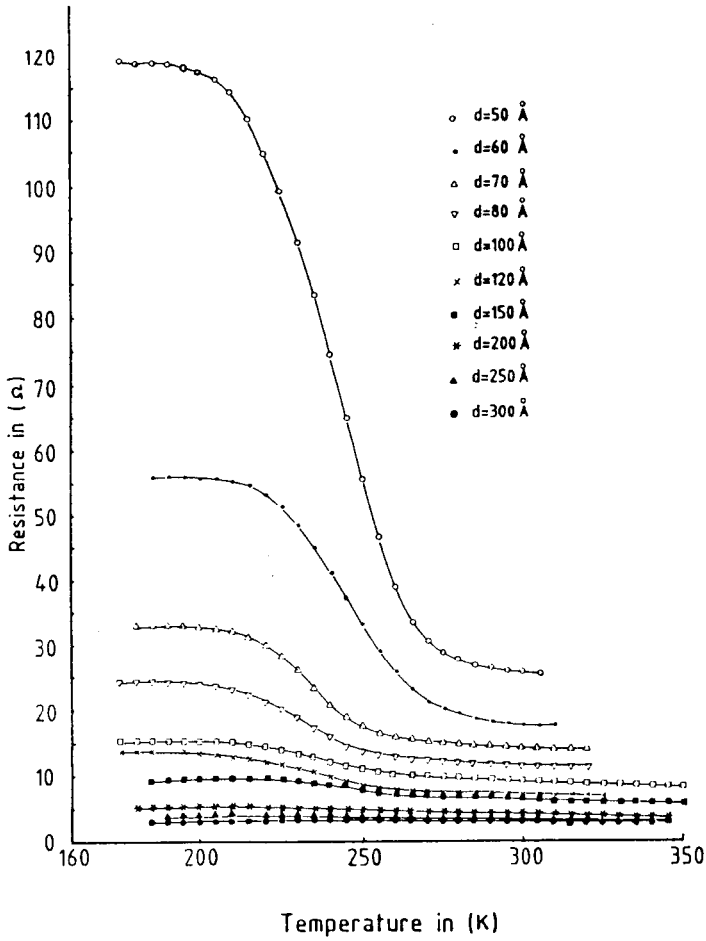

Fig. 1: Annealing curves for Ag films deposited at 175 K.

It is obvious from Figure 1 that annealing has more profound effect particularly for films with smaller thicknesses and or low desposition temperatures (T_d). This is due to the fact that thinner films deposited at low T_d have geometrical defects which could be decreased by annealing.

Among the factors affecting the film morphology and topography are the substrate temperature, film thickness and subsequent film annealing (Thun 1969). Since the substrate temperature determines the mobility of the condensate atoms, then at low substrate temperatures, surface self-diffusion is negligible. This means that the film will be composed of columnar crystallites separated by gaps (Albano *et al.*

1985, Mc Breen and Moskovits 1983).

Thinner films deposited at low temperatures are expected to be composed of smaller crystallites and hence larger grain boundaries. Accordingly they will exhibit higher resistance values. On raising the film temperature, surface self-diffusion becomes appreciable and diffusing atoms will fill the narrow gaps and thus normal grain boundaries are formed (Albano et al 1985, Mc Breen and Moskovits 1983).

It has been reported that the structure of Ag films deposited at 90 K contained trenches (Gimzewski et al 1985) which resemble the pores exhibited in Ag films deposited at 58 K (Albano et al 1983). Albano et al (1983, 1985) reported that such pores disappeared upon annealing at temperatures $>$ 170 K. Accordingly the observed decrease in the resistance values reported in this work, due to annealing, might be due to the reduction in grain boundaries. Hence the contribution to the resistance from grain boundary scattering could be minimal.

After reaching minimum values in the films' resistances due to annealing, reversible changes in the resistances were observed when the films were subjected to cooling and heating cycles. This almost linear reversible changes in the resistances is in agreement with that obtained by Schlemminger and Stark (1986) for Ag films.

2. Temperature Coefficient of Resistance (TCR)

The values of β could be determined from the variation in the resistance with temperature using the equation:

$$\beta = \frac{1}{R}\frac{dR}{dT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

From the data reported in the previous section, the variation of β with thickness was determined.

The general behaviour of the thickness dependence of β as shown in Figure 2 is the same for the investigated temperature range. A sharp increase in β is observed with increasing thickness up to about 200 Å, then β approaches a limiting value which depends on the deposition temperature. This behaviour is similar to that obtained for palladium (Wedler and Alshorachi 1980), strontium (Renucci et al 1983) and Cu - Ag films (Reda et al 1984). Also, low values of β were obtained for films deposited at low temperatures. This indicates that the contribution of thermal scattering to the film resistance is small compared with that of structural disorder (Reda *et al* 1984).

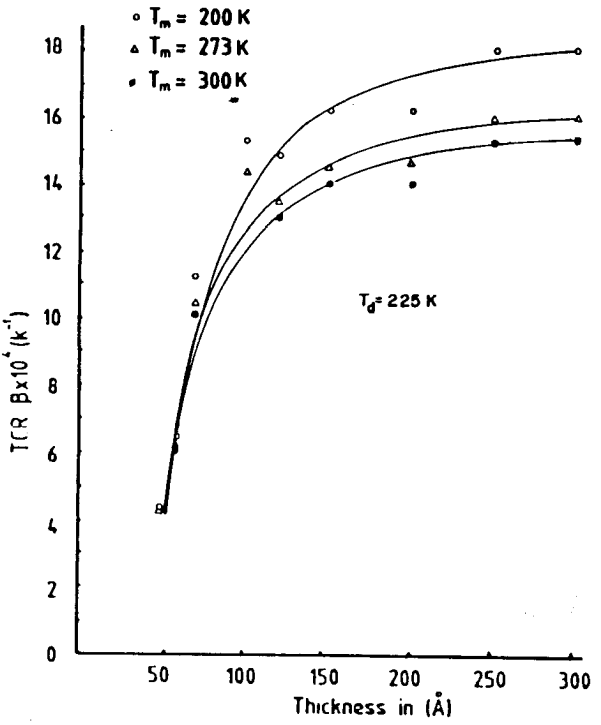

Fig. 2: Variation of the TCR (β) of Ag films with thickness.

The value of the TCR for a film of infinite thickness (β_∞) was determined from the slope of the graph β d versus d (Chopra 1976, Renucci et al 1985).

However, Wedler and Alshorachi (1980) reported that β for Pd films was not linear in l/d since d is of the order of the bulk mean-free path ℓ_∞. Nevertheless, FS approximate equation for thick films was used to fit experimental data with $d/\ell_\infty \geq 0.1$ (Wedler and Chander 1980, Schlemminger and Stark 1986, Al-Houty and Arrubban to be published).

Figure 3 shows an example of the obtained behaviour of the variation of β d versus d. It is obvious that β is linear in l/d for Ag films. The values of β_∞ corresponding to various measuring temperatures T_m are listed in Table 1.

Table 1

TCR (β_∞) values at various temperatures

T_d(K)	225			275		
T_m(K)	200	273	300	200	273	300
β_∞ x 10^3 (K^{-1})	2.08	1.84	1.75	3.44	2.85	2.65

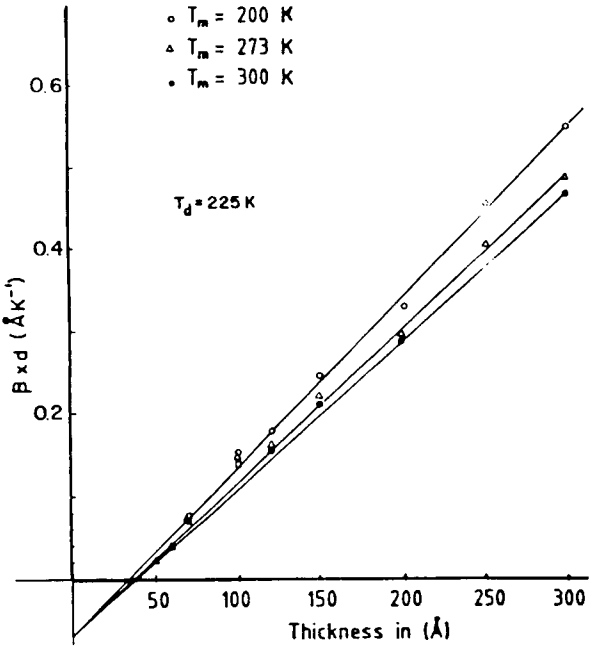

Fig. 3: Variation of βxd with d for Ag films.

For films deposited at the same temperature, β_∞ decreases with increasing temperature. This result is similar to that obtained for strontium films (Renucci et al 1983).

3. The defect Density

In Vand's theory (Vand 1943), the irreversible changes in the film resistance with temperature are attributed to the decay of the defects or distortions such as vacancies and interstatials. If distortions of various decay energies E_o are included in the films, then the resistance changes due to heat treatment are given by:

$$R_i(t) = \int_{E_o(t)}^{\infty} F_o(E_o)\, dE \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where $F_o(E_o)$ is a characteristic function of the film and represents the distribution of the distortions as a function of their decay energies E_o and given by:

$$F_o(E_o(t)) = \frac{-at}{E_o} \quad \frac{E_o + Kat}{E_o + 2Kat} \quad \frac{dR_i(t)}{dT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where the rate of increase in temperature $a = \frac{dT}{dt}$ and k Boltzman constant.

In this work, Mathissen's rule was used as a good approximation to estimate $\frac{dR_i}{dT}$. Since $R = R_i + R_T$, where R_T represents the contribution from lattice vibrations and R_i the resistance due to defects. Then:

$$\frac{dR}{dT} = \frac{dR_i}{dT} + \frac{dR_T}{dT}$$

At a given temperature, $\frac{dR}{dT}$ was obtained from the first annealing curves (Figure 1). while $\frac{dR_i}{dT}$ was obtained from the linear curves.

The experimental results reported in Section (1) were used to obtain $\frac{dR_i}{dT}$. A computer program was used to compute the variation of F_o (E_o) as a function of E_o (Equation 3). The results obtained for Ag films of different thicknesses deposited at 175, 225 and 273 K are shown in Figures 4 & 5.

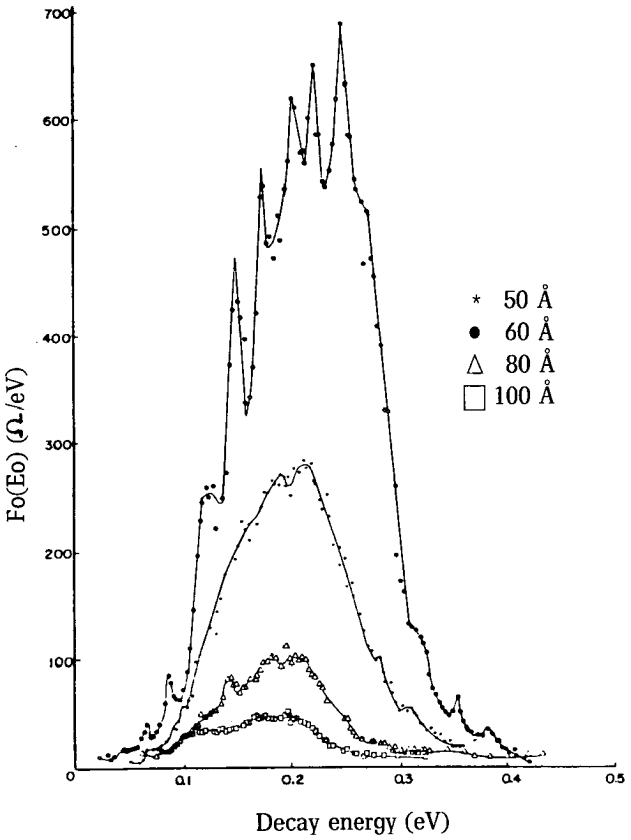

Fig. 4: Lattice distortion energy spectrum of Ag films deposited at 175 K.

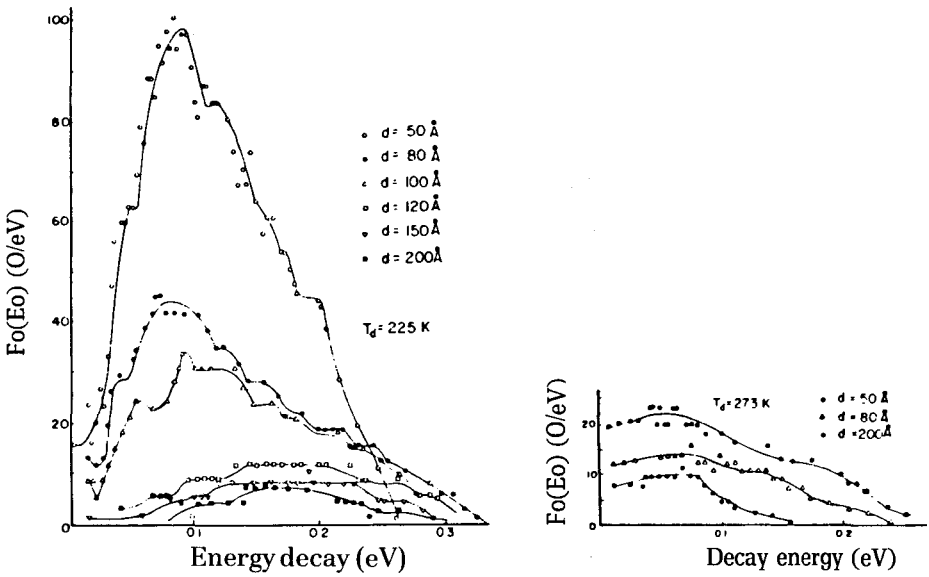

Fig. 5: Lattice distortion energy spectrum of Ag films deposited at 225 and 273 K.

It can be seen that the behaviour of F_o (E_o), a measure of the density of defects in the film, depends on the deposition temperature as well as the film thickness. A sharp peak is observed for films deposited at 175 and 225 K and having thicknesses < 150 Å and < 100 Å respectively. While the curves have no obvious maxima for films of thicknesses larger than the above mentioned values and for all films deposited at 273 K. Also, the value of F_o (E_o) at the maximum is greater for very thin films and/or low deposition temperature. Accordingly, thin films deposited at low temperatures are expected to exhibit higher resistivity values. The dependence of the Vand function F_o on the energy E_o for a 50 Å film deposited at 175 K shows several peaks. This means that several defects disappear during annealing. Similar results were obtained for strontium films of thicknesses greater than 1200 Å. (Renucci et al 1985).

At a certain deposition temperature the maximum value of F_o (E_o) decreases with increasing film thickness which is in agreement with Vand's theory. Similar results were also obtained for silver (Flechon et al 1976), calcium (Renucci *et al* 1982), magnesium (Renucci et al 1985) and strontium (Renucci *et al* 1985).

The activation energy, that is the energy of the maximum, decreases with increasing deposition temperature. The activation energy was equal to 0.2 eV for films deposited at 175 K, irrespective of film thickness. This thickness independent behaviour is similar to that obtained for calcium films (Renucci et al 1982). However, films deposited at 225 K show a

slight thickness dependence of the activation energy which is in agreement with previous results reported for magnesium (Renucci et al 1985). The activation energy of such films is about 0.1 eV for $d \leqslant 100$ Å.

The activation energy values obtained in this work are in agreement with the values of 0.17 - 2.0 eV reported by Kepinski (1981). The structure of those films (Kepinski 1981) varied from island-like to quasi-continuous and for the thinnest films, the particle density decreased with increasing thickness. However, these values are completely different from the value of 1.12 eV reported by Flechon et al (1976) for Ag films prepared by chemical reduction. The discrepancy in the results might be due to the difference in the methods of film preparation.

The variation of the maximum in the Vand function F_o $(E_o)_{max}$ with thickness for films deposited at 175 and 225 K show two different linear behaviour, while those deposited at 273 K follow only one line. The variation in F_{max} is fairly steep in the first linear part that corresponds to very thin films deposited at 175 and 225 K. While the slopes of the lines are small for thicker films as well as all films deposited at 273 K. This indicates that films deposited at 273 K having $d > 50$ Å together with films having $d > 150$ Å deposited at low temperatures > 175 K exhibit minimum defects in their structure. The behaviour of F_{max} showing two linear parts is similar to that obtained for magnesium (Renucci et al 1985); while that showing one linear part is similar to that obtained for silver (Flechon et al 1976).

The experimental results and analysis presented in this work showed that cold-deposited Ag films exhibit irreversible resistance changes upon annealing. It is well known that excess vacancies and interstatials can be created as a result of cold work or irradiation by energetic particles (Corbett 1966, Elliott and Gibson 1974). These point defects are usually frozen in the crystal and can move very slowly to the surface by diffusion.

The energy necessary to create a vacancy E_v is less than the energy E_I required to create an interstatial. Also, the activation energy for the motion of interstatials is often much smaller than that for vacancies; hence, they diffuse out of a crystal much more readily than vacancies (Elliott and Gibson 1974). Accordingly, cold-evaporated films followed by mild annealing would favour the generation of vacancies.

Pockrand and Otto (1981) attributed the increase of the Raman intesities of Ag films to the increase of the density of effective point defects (e.g. divacancies) or a transformation of less effective to more effective ones. They also suggested that unstable vacancy clusters might discociate into divacancies or divacancies might seperate from dislocations or grain boundaries.

It is suggested that the irreversible decrease in the resistance of Ag-films might be due to different mechanisms depending on the substrate temperature (Figures 4 and 5). The activation energy value of 0.2 eV obtained for films deposited at 175 K agrees with that reported (0.18-0.2 eV) for stage 2 recovery after cold work or deuteron-irradiation of bulk

silver (Corbett 1966). In such films, the observed change in the resistance might be due to the mirgation of divacancies and interstatials.

For films deposited at 225 K, the observed change might be due to free migration of an interstatial and to close-pair recovery. Hence the obtained activation energy of 0.1 eV supports stage 1 recovery. (Figure 5).

CONCLUSION

The study of silver films of thicknesses 50 - 300 Å deposited onto cooled glass substrates showed that the behaviour of the electrical properties depends on the thickness region as well as the deposition temperature. Films having thicknesses less than 150 A and deposited at temperatures < 225 K show high resistance and defect density values. It is proposed that films deposited at $T_d < 225$ K exhibit two types of structure depending on the thickness region. The thinnest films are discontinuous, then a change in the structure occurs for films with $d \simeq 150$ Å. Above this thickness, the films show a continuous behaviour.

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سلوك التخمر البطيء ـ قيم المعامل الحراري للمقاومة ـ كثافة التشوه لأغشية رقيقة من الفضة (باردة الترسيب)

لطيفة ابراهيم الحوطي و موزة محمد الربان

تمت هذه الدراسة على أغشية رقيقة من الفضة تم تحضيرها بطريقة التبخير تحت ضغط منخفض يبلغ حوالي ١٠ $^{-٦}$ مم زئبق حيث كان الوسط المحيط بالعينة معبأ بغاز الأرجون (الخامل) . كما رسبت تلك الأغشية على سطوح زجاجية محفوظة عند درجات حرارة منخفضة . تناولت الدراسة عمليات التخمر البطيء على المقاومة الكهربية وكذلك كثافة التشوه في أغشية الفضة الرقيقة .

تبين من تحليل النتائج باستخدام نظرية فاند Vand أن تغير دالة فاند F_o ـ كمؤشر لكثافة التشوة ـ مع تغير طاقة الاضمحلال يعتمد على كل من سمك الغشاء ودرجة حرارة الترسيب . وقدرت طاقة التنشيط لأغشية الفضة بحوالي 0.1 و 0.2 الكترون فولت للأغشية المرسبة عند ٢٧٥ ، ٢٢٥ درجة مطلقة على الترتيب . كما تبين أن طاقة التنشيط تتغير بسيطاً مع سمك الغشاء حتى حوالي ١٢٠ انجستروم وذلك لدرجة حرارة ترسيب ٢٢٥ درجة مطلقة .

كما بينت الدراسة أن قيمة المعامل الحراري للمقاومة لغشاء ذو سمك لا نهائي يعتمد على درجة حرارة الترسيب .