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# Ageing studies of discontinuous copper and silver thin films

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The results of experiments carried out on the post-deposition resistance changes in discontinuous films of copper and silver with and without overlayers of SiO and $Al_2O_3$ are presented. The changes in the sheet resistance of the films with time and pressure were studied for the above combinations. Mobility coalescence is assumed to be responsible for the resistance increase of an uncovered copper film of initial resistance 1.9 MΩ/□. On exposure to the atmosphere, it was found that an Ag/SiO combination of initial resistance of 0.1 MΩ/□ achieved stability in the sheet resistance much quicker than a Cu/$Al_2O_3$ combination of initial resistance 20 MΩ/□. The fall in resistance of the Cu/$Al_2O_3$ composite is attributed to the formation of $Al_2(OH)_6$ due to the interaction of $Al_2O_3$ with the water vapour in atmosphere. Copper films with and without overlayers of $Al_2O_3$ show an abrupt increase in the sheet resistance as a function of pressure at a pressure of about $5 \times 10^{-2}$ torr with the maximum rate of change of resistance occurring at higher pressure for the higher resistance film. This indicates that the overlayer of $Al_2O_3$ is very porous in nature. Field effect studies were carried out on an uncovered copper film of initial resistance 10 MΩ/□ and the behaviour was found to be ohmic up to a field of 800 V cm$^{-1}$.

## 1. Introduction

Discontinuous metal films have great potential as high sensitivity strain gauges due to their high gauge factor. Gauge factors (defined as the ratio between the relative resistance change ($\Delta R/R$) and the fractional deformation ($\Delta l/l$)) between 10 and 200 [1–4] have been reported. The main obstacle to practical applications of discontinuous films is the instability of their physical properties. This instability is seen as an increase in the sheet resistance with time. Many theories have been put forward to explain this resistance increase. Skofronick and Phillips [5] attributed the resistance increase to agglomeration of islands on the substrate surface which increases the average inter-island spacing. Morris [6] suggested that the resistance increase could be due to reduced electron emission due to a decrease in the film temperature following removal of the heating effect of the radiant source. Paulson and Friedberg [7] through an investigation of gas adsorption, obtained results similar to those of Skofronick and Phillips [5]. Nishiura and Kinbara [8] have attempted to explain the resistance increase following deposition on the basis of the change in island shape from an originally rotational ellipsoid form to a spherical form, thus increasing the average inter-island spacing. Fehlner [9], Erhlich [10] and Deshpande [11] assumed that oxidation of the metal islands causing an increase in the average inter-island spacing and a change in the work function was responsible for the increase in resistance with time for discontinuous films.

Many attempts have been made to improve the temporal stability of discontinuous thin films. With a view to reducing agglomeration by reducing the movement of the individual islands over the substrate, substrates have been damaged with radiation [12]. The discontinuous films have also been coated with overlayers of SiO [12, 13] and $Al_2O_3$ [13] to prevent their interaction with atmospheric gases, but the stability has not improved to a great extent. This paper reports the results of experiments carried out in our laboratory on the post-deposition resistance changes in discontinuous films of copper and silver with and without overlayers of SiO and $Al_2O_3$. This was with a view to obtaining a stable film for strain gauge fabrication.

## 2. Experimental details

Discontinuous copper films of initial resistance 1.9 and 10 MΩ/□, a Cu/$Al_2O_3$ film of resistance 20 MΩ/□ and an Ag/SiO film of initial resistance 0.1 MΩ/□ were vacuum deposited at a pressure of $8 \times 10^{-6}$ torr on to clean glass substrates held at room temperature. The resistance of the film was monitored during deposition using a Keithley electrometer. A shutter arrangement was employed to stop the deposition as soon as the desired resistance was obtained. All the copper films had dimensions of 0.5 cm × 0.5 cm while the Ag/SiO film was 1 cm × 1 cm. The source-to-substrate distance was 20 cm. Thick contacts of the metal to be studied were deposited at the ends of the substrate and pressure contacts made from which leads were taken for resistance monitoring. The glass plates used as substrates were cleaned with warm chromic acid, detergent solution and distilled water, in that order.



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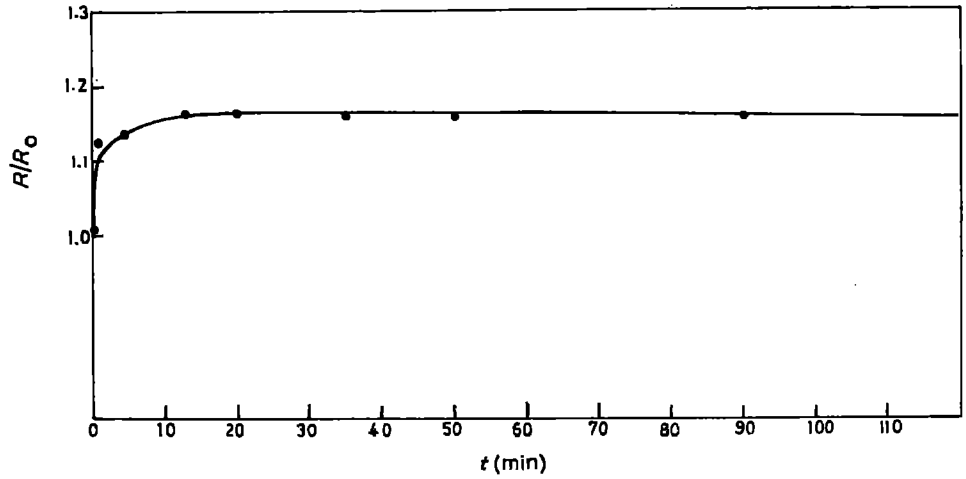


*Figure 1* Normalized resistance plotted against time for a copper film of $R_0 = 1.9\,\mathrm{M\Omega/\square}$ in vacuum.

Immediately before mounting the substrates in the deposition chamber, they were finally cleaned with isopropyl alcohol and distilled water. Glow discharge was used for a period of 7 to 10 min before depositing the discontinuous film to rid the substrate surface of water vapour and adsorbed gases. The silver and copper used in this study were of 99.999% purity. During deposition of the films, the boat current was held steady and constant to maintain a constant deposition rate. $Al_2O_3$ and SiO were deposited on to the discontinuous film using an electron gun arrangement. In all cases, the film resistance was allowed to stabilize, before depositing the overlayer. Field effect studies were carried out on a copper film of initial resistance $R_0 = 10\,\mathrm{M\Omega/\square}$ after the film resistance had stabilized and drift in the resistance could be ruled out.

For a copper film of $R_0 = 1.9\,\mathrm{M\Omega/\square}$, ageing studies were carried out in vacuum. After the film resistance had stabilized, it was studied as a function of pressure. The pressure in the chamber was regulated using a sensitive needle valve arrangement. The pressure dependence of the resistance was also studied for a copper film of $R_0 = 10\,\mathrm{M\Omega/\square}$ prior to which field effect studies in the range 10 to $800\,\mathrm{V\,cm^{-1}}$ were carried out. The dependence of the sheet resistance of a $Cu/Al_2O_3$ film of $R_0 = 20\,\mathrm{M\Omega/\square}$ on pressure was studied after which the film was aged in the atmosphere. Finally, the resistance of an Ag/SiO film of $R_0 = 0.1\,\mathrm{M\Omega/\square}$ was studied in vacuum and at atmospheric pressure as a function of time.

## 3. Results and discussion

Fig. 1 shows the variation of the normalized resistance with time for a copper film of $R_0 = 1.9\,\mathrm{M\Omega/\square}$ with the resistance becoming stable after a period of 15 min. Fig. 2 shows the variation of the normalized resistance with the logarithm of the pressure (ln $P$) for copper films of $R_0 = 1.9$ and $10\,\mathrm{M\Omega/\square}$. It is seen that the maximum rate of change of resistance with pressure occurs at a higher pressure for the $10\,\mathrm{M\Omega/\square}$ film. The dependence of the logarithm of the resistance on the square root of the applied field for the $10\,\mathrm{M\Omega/\square}$ copper film is shown in Fig. 3. It is evident that the film is ohmic in nature up to a field of $800\,\mathrm{V\,cm^{-1}}$. The

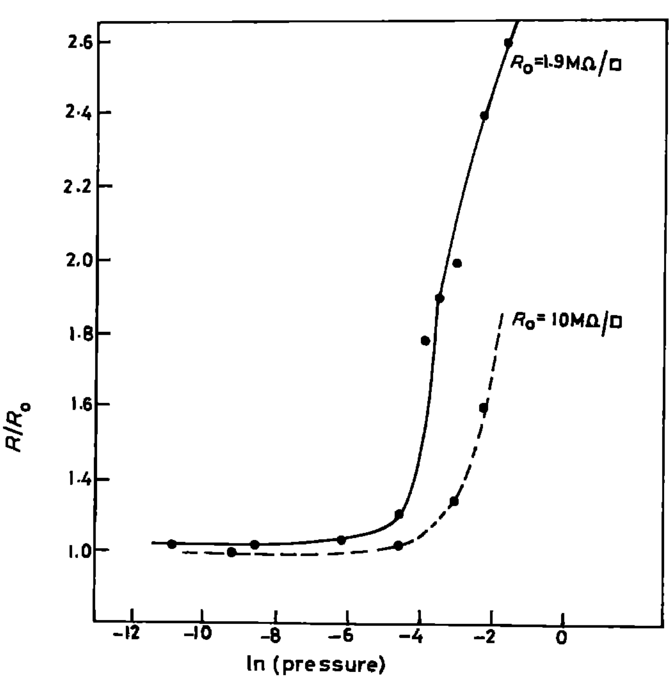


*Figure 2* Normalized resistance plotted against ln ($P$) for copper films of $R_0 = 1.9$ and $10.0\,\mathrm{M\Omega/\square}$.

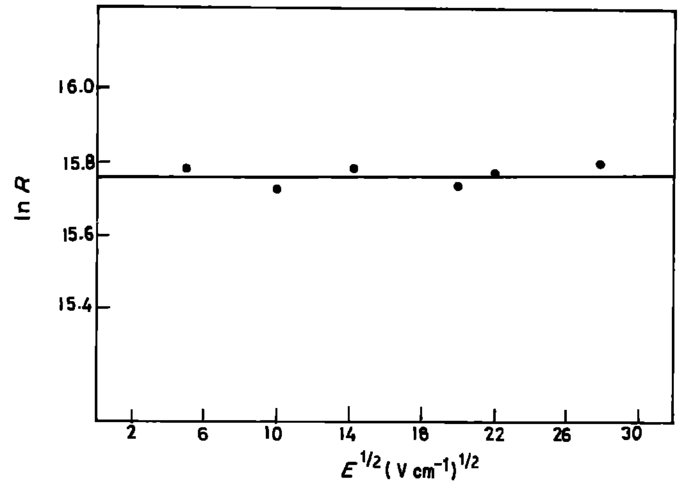


*Figure 3* ln ($R$) plotted against $E^{1/2}$ for a copper film of $R_0 = 10.0\,\mathrm{M\Omega/\square}$.

variation of the normalized resistance with ln $P$ for a $Cu/Al_2O_3$ film of $R_0 = 20\,\mathrm{M\Omega/\square}$ is shown in Fig. 4. The same $20\,\mathrm{M\Omega/\square}$ film was exposed to the atmosphere and the time variation of the normalized resistance is shown in Fig. 5. There is a small increase in the normalized resistance followed by a steady fall with the resistance not stabilizing even after 100 min. The Ag/SiO composite of $R_0 = 0.1\,\mathrm{M\Omega/\square}$ was aged in vacuum and the atmosphere. The time dependence of the Ag/SiO film is shown in Fig. 6. In contrast to the $Cu/Al_2O_3$ film, the Ag/SiO film exposed to the atmosphere attains a stable configuration within the first 20 min.

The quantum-mechanical tunnelling model gives the expression for resistance of a discontinuous film to be [14]

$$R = f(d) \exp [4\pi d/h(2m\phi)^{1/2}] \tag{1}$$

where $R$ is the resistance of the film, $f(d)$ is a slowly varying function of $d$, the average inter-island spacing, $\phi$ is the effective tunnelling barrier between the islands, and all other symbols have the usual meaning.

An increase in the average inter-island spacing could explain an increase in the resistance with time (Equation 1) as observed by us (Figs 1 and 6). This increase in the average inter-island spacing could come about by the following mechanisms.

Discontinuous films ideally consist of an array of islands with a statistical distribution of island spacings [15–17]. Kinosita [18], in a paper which gives the historical development of the theory of mobility coalescence, has shown that mobility of large islands must be included in the Zinsmeister rate equations to explain the shape of the experimentally observed island size distribution curve. The binding energy for copper on glass is $E_{des} = 0.14\,\mathrm{eV}$ [19]. The energy for surface diffusion of Cu adatoms on the surface is therefore $E_d = E_{des}/4 = 0.035\,\mathrm{eV}$ [20]. In the absence of data for silver, we shall assume that the energy for surface diffusion is, at worst, equal to that of copper; in all probability it will be less than for copper. In the light of the above values, it is reasonable to assume that small islands exist in the copper and silver films which move, coalesce and cause an increase in the average inter-island spacing and consequently, the resistance of the film. This we observe for the $1.9\,\mathrm{M\Omega/\square}$ copper film and the Ag/SiO film of $R_0 = 0.1\,\mathrm{M\Omega/\square}$ (see Figs 1 and 6, respectively). In the case of silver, slow coalescence takes place in spite of the SiO overlayer indicating that the smaller silver islands are extremely mobile.

Figs 2 and 4 show that there is a sudden increase in the resistance of the film in a well-defined pressure interval. This is due to fast oxidation taking place at this critical pressure ($\simeq 5 \times 10^{-2}$ torr) which makes the change in resistance measurable in the time scale used. An overlayer of $Al_2O_3$ in the case of the $Cu/Al_2O_3$, $20\,\mathrm{M\Omega/\square}$ film does not significantly affect the pressure dependence of the resistance. This is due to the porous nature of the $Al_2O_3$ overlayer which is unable to prevent the oxidation of the copper islands. The oxidation of the islands leads to an increase in the average inter-island spacing and hence, the resistance [9–11]. The view that the $Al_2O_3$ overlayer is porous is strengthened when one looks at the resistance behaviour of the $Cu/Al_2O_3$ $20\,\mathrm{M\Omega/\square}$ film exposed to the atmosphere (Fig. 5). The initial resistance increase up to a period of 8 min is due to continued oxidation. $Al_2O_3$ is known easily to form $Al_2(OH)_6$ in combination with moisture. $Al_2(OH)_6$ provides $OH^-$ ions which are mobile and contribute significantly to the conductivity. This results in a fall in the resistance. In the humid conditions of Madras, this is a most probable mechanism with the process continuing for 100 min. The resistance does not stabilize even at the

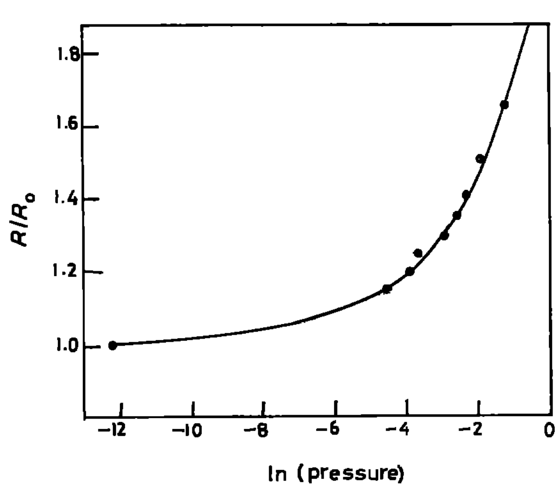


*Figure 4* Normalized resistance plotted against ln ($P$) for a $Cu/Al_2O_3$ film of $R_0 = 20.0\,\mathrm{M\Omega/\square}$.

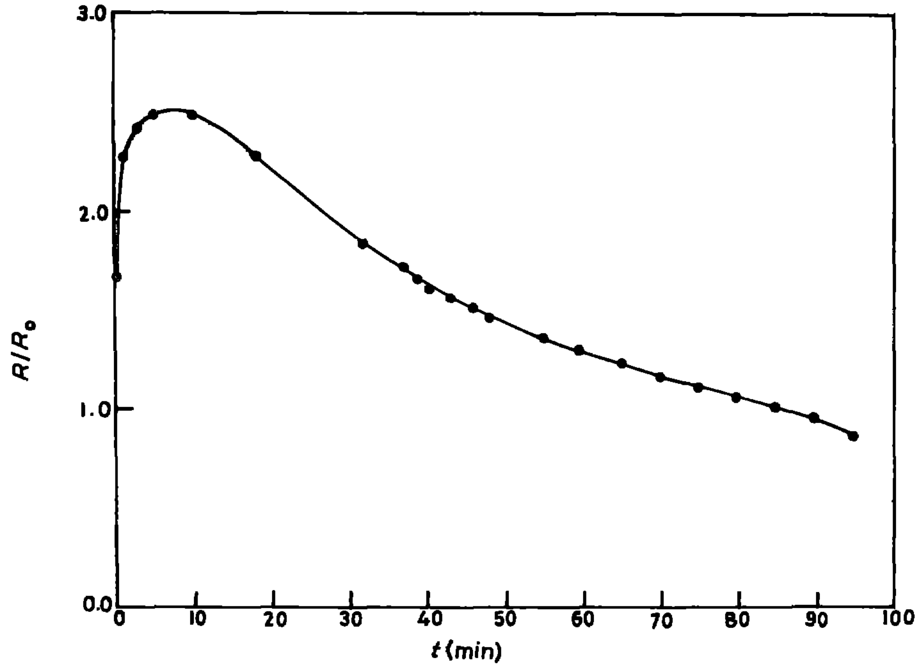


*Figure 5* Normalized resistance plotted against time for a $Cu/Al_2O_3$ film of $R_0 = 20\,M\Omega/\square$ in the atmosphere.

end of that period. In the case of the Ag/SiO film exposed to the atmosphere, the initial fall in the resistance is due to occlusion of gases on the surface of the SiO overlayer. Once the process of occlusion is over, the film resistance stabilizes (Fig. 6). Following Neugebauer and Webb [14], we studied the field effect of a discontinuous copper film of $R_0 = 10\,M\Omega/\square$ over the field range 10 to $800\,V\,cm^{-1}$ and found that the film was ohmic in this region (Fig. 3).

## 4. Conclusions

1. Discontinuous films of copper with and without overlayers of $Al_2O_3$ oxidize in a well-defined pressure interval with the point of maximum rate of change of resistance with pressure increasing with increasing initial resistance of the film.

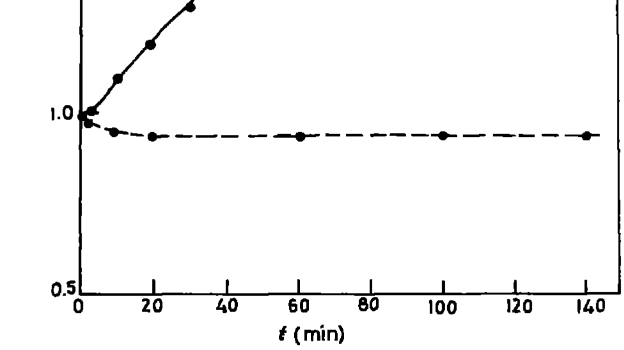


*Figure 6* Normalized resistance plotted against time for Ag/SiO film of $R_0 = 0.1\,M\Omega/\square$ in vacuum and the atmosphere. (——) Ageing in vacuum, (---) ageing in the atmosphere.

2. Mobility coalescence was responsible for the increase in the resistance of a copper film of $R_0 = 1.9\,M\Omega/\square$ and an Ag/SiO film of $R_0 = 0.1\,M\Omega/\square$.

3. The $Al_2O_3$ overlayer of a $Cu/Al_2O_3$ film of $R_0 = 20\,M\Omega/\square$ forms a hydrate resulting in a contribution to the film conductivity and hence, a fall in the resistance.

4. SiO was found to be a good passivating agent with an Ag/SiO film of $R_0 = 0.1\,M\Omega/\square$ attaining stability in the atmosphere within a short time. $Al_2O_3$ provided a porous overlayer and inadequate protection against water vapour and oxidation.

5. Field effect studies carried out on a copper film of $R_0 = 10\,M\Omega/\square$ showed that the film was ohmic in nature up to a field of $800\,V\,cm^{-1}$.

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