

Studies on the stability of Cu island films deposited on a softenable substrate

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Studies on the stability of Cu island films deposited on a softenable substrate

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In this communication, we report the results of the investigations carried out on the stability of discontinuous Cu films deposited on polymethylmethacrylate coated substrate heated to a temperature above the glass transition temperature of the polymer. It was reported that evaporated materials on such substrates form a subsurface particulate structure. It was found that in Cu films post-deposition instability persisted on a softenable substrate similar to the behavior of Cu on glass. On exposure to atmosphere, the resistance increased due to the interaction of atmospheric gases and water vapor. A film deposited at room temperature and heated also behaved in a similar fashion when exposed to atmosphere.

The instabilities in physical properties of discontinuous metal films is attributed to various causes.^{1–3} It is generally accepted that mobility of islands followed by coalescence is responsible for the post-deposition instability in such films, which is further strengthened by electron microscopic studies.³ There had been attempts to reduce this instability by damaging the substrate surface with radiation⁴ and by depositing insulating overlayers,^{4–6} but with these techniques long-term stability could not be achieved. Recently, formation of a subsurface particulate film were reported, when some elements were vacuum deposited onto soft substrates.^{7–10} These structures are similar to discontinuous films, with a difference that they are formed below the substrate surface. It was expected that if such a structure could be attained with metal particles dispersed as a monolayer beneath the substrate surface, it would result in a stable cermet-like structure. Electrical properties of such systems are yet unexplored. If a stable high-resistance film is attained with such a structure it can be used for device applications such as high value resistors and high sensitivity strain gauges. In this communication, we report the results of the study carried out on the copper island films deposited on polymethylmethacrylate (PMMA) coated substrates held at a temperature above the softening temperature of PMMA and also a film coated at room temperature and subsequently heated to the softening temperature of the polymer.

Discontinuous films of copper with initial resistances

(resistance immediately after the stoppage of deposition) $R_0 = 9.0, 2.0,$ and $0.2 \text{ M}\Omega/\square$ were deposited onto glass substrates coated with PMMA held at 423 K in a vacuum of 1×10^{-5} Torr. Thick copper contacts were coated on glass substrates with $2.5 \text{ cm} \times 2.5 \text{ cm}$ gap at the center. PMMA is solution coated between the copper contacts. Thin copper leads were soldered to the contacts for resistance measurements. The substrate-to-source distance was 20 cm. Resistance measurements were done with a Keithley electrometer. A copper-constantan thermocouple clamped to the substrate surface holding the film was used to measure the temperature. A shutter arrangement was employed to stop the deposition at the required resistance. The polymer, PMMA, was found to soften at about 378 K (T_g) which is in agreement with the reported value.¹¹ The substrates were kept at 423 K, well above T_g , during deposition for the three films of $R_0 = 9.0, 2.0,$ and $0.2 \text{ M}\Omega/\square$ and annealed at that temperature for one hour. The deposition rate was 0.4–0.6 nm/s. The films were then cooled to room temperature before exposing to atmosphere. Furthermore, one film of $R_0 = 0.29 \text{ M}\Omega/\square$ was deposited at room temperature and heated to 423 K after aging for 1 h. The film was then cooled and exposed to atmosphere.

Figure 1 shows the variation of normalized resistance with time for the films deposited at 423 K. In the inset, variation of normalized resistance with time for a film of $R_0 = 0.29 \text{ M}\Omega/\square$ at room temperature is shown. It can be

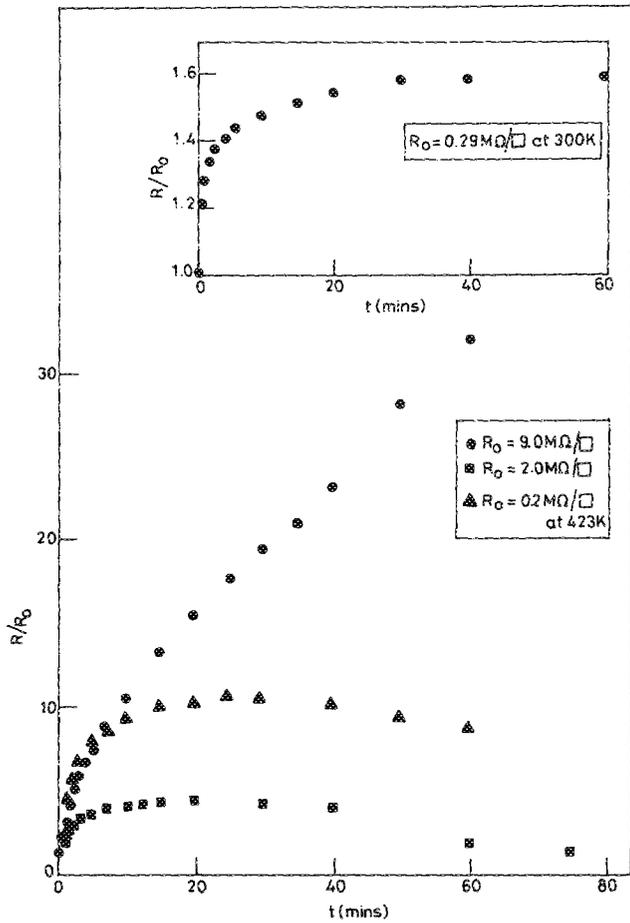


FIG. 1. Variation of normalized resistance with time for films at 423 K and a film at room temperature.

seen that for the film at room temperature the resistance variation is much less compared to the film of almost the same resistance at 423 K. Figure 2 shows the variation of normalized resistance with the logarithm of pressure for the films deposited at 423 K and cooled to room temperature during exposure to atmosphere. It is clear from the figure that for all the films there is a sharp increase in resistance at near atmospheric pressure. In Fig. 3, the variation of the logarithm of resistance with $1/T$ is shown for a film of $R_0 = 0.29 \text{ M}\Omega/\square$ at room temperature during heating and cooling cycles. From the figure, two regions of resistance decrease and increase can be seen. The resistance increase starts around 360 K. During cooling an initial increase followed by almost steady behavior is seen. This film, when exposed to atmosphere behaved similar to the ones shown in Fig. 2.

When inorganic materials are deposited onto organic polymer substrates heated to a temperature above the glass transition temperature T_g , subsurface particulate monolayers are thermodynamically preferred.⁷ Based on the surface free energies of the system favorable condition for such a structure to be formed is given by⁸

$$\gamma_1 > \gamma_2 + \gamma_{12},$$

where γ_1 and γ_2 are surface tensions of the particle and substrate, respectively. γ_{12} is the interfacial tension between the substrate and particle. The same inequality also holds good for the complete immersion of the particles whether they are growing during vacuum deposition or preformed particles on a substrate subsequently softened. It is further reported that the inequality generally holds well for an organic polymer and inorganic evaporant.⁹ If such a structure is formed, the islands being immersed in the polymer a few tens of nanometers below the surface, it is expected that the polymer covering would prevent any interaction of the metal particles with the atmospheric gases when exposed to atmo-

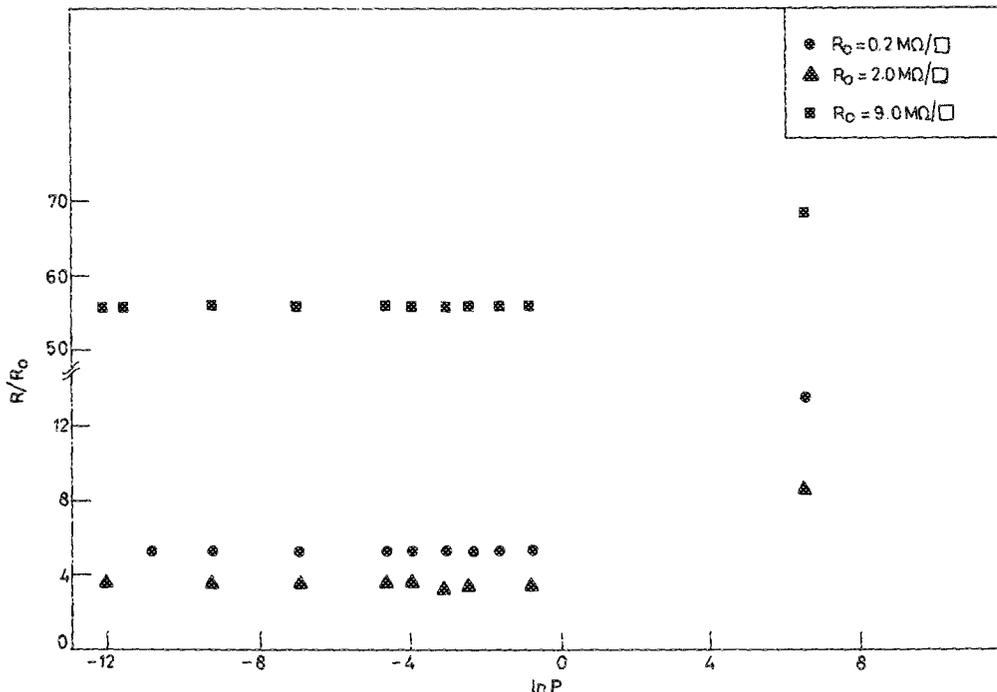


FIG. 2. Variation of normalized resistance with \ln (pressure) during exposure to atmosphere.

sphere, but from Fig. 2 it can be seen that this is not the case. A similar behavior was observed by us earlier with overlay coatings.⁶ The film which was deposited at room temperature and heated beyond the softening temperature of the polymer also showed similar behavior indicating that the copper islands did not sink into the softened substrate and that such a subsurface structure has not been formed.

A limiting condition for the formation of subsurface structure is the deposition rate and growth mode. The transition from island (Volmer-Weber) to Stranski-Krastanov (layer-by-layer) mode will prevent the particle sinking. Also, if the deposition rate is higher than the sinking rate subsurface particulates will not be formed.⁷ In our case, the deposition rate was only 0.4–0.6 nm/s and hence, its effect can be ruled out. From Fig. 1, we can see that the resistance increases with time and for two films of $R_0 = 2.0$ and $0.2 \text{ M}\Omega/\square$ the increase is followed by a small fall in resistance after long times. As the thickness of the film increases, the island size distribution shifts towards the higher average island size and the surface coverage increases resulting in a reduction of the average interisland spacing. The average interisland spacing determines the film resistance.¹² Hence, thicker films will have lower R_0 than the thinner films. Mobility of an island is a thermally activated process and also, smaller islands are more mobile as compared to larger islands. Mobility of islands followed by coalescence leads to an increase in the interisland spacing³ and hence, the film resistance. It is observed (Fig. 1) that the rate of resistance increase is larger for higher R_0 films than the lower R_0 films. Also, at higher temperatures the rate of resistance increase is larger than at room temperature for almost the same initial resistance films, consistent with the thermally activated mobility coalescence model. The fall in resistance after a long time in two of the cases can be explained as follows. At a particular temperature the island distribution changes with time due to mobility coalescence and attains an equilibrium distribution. The time taken to reach the equilibrium is larger for higher R_0 films (smaller islands) than the lower R_0 films (larger islands). Once the distribution of islands attain equilibrium the islands may flatten out on a soft substrate resulting in the reduction of average interisland spacing hence, the film resistance. In the case of film of $R_0 = 9 \text{ M}\Omega/\square$ the equilibrium is not reached even after 60 min and, hence, the reduction in resistance was not observed in that period. From the above-mentioned results it is clear that the film consists of islands and we can say that the S K growth mode is not operative in this case. The other kinetic factor limiting the formation of subsurface particulate structure is the substrate temperature.⁹ For the polymer used, PMMA, the substrate temperature cannot be raised beyond 430 K because the polymer degradation starts at temperatures beyond 430 K.

The resistance temperature characteristics (Fig. 3) may be explained as follows. The initial negative TCR region is characteristic of discontinuous films. The resistance increase beyond 360 K is due to the activated movement of islands, followed by coalescence.¹³ It should be noted that the resistance increase starts around 360 K, which is below the softening temperature of the polymer (378 K). Hence, the resis-

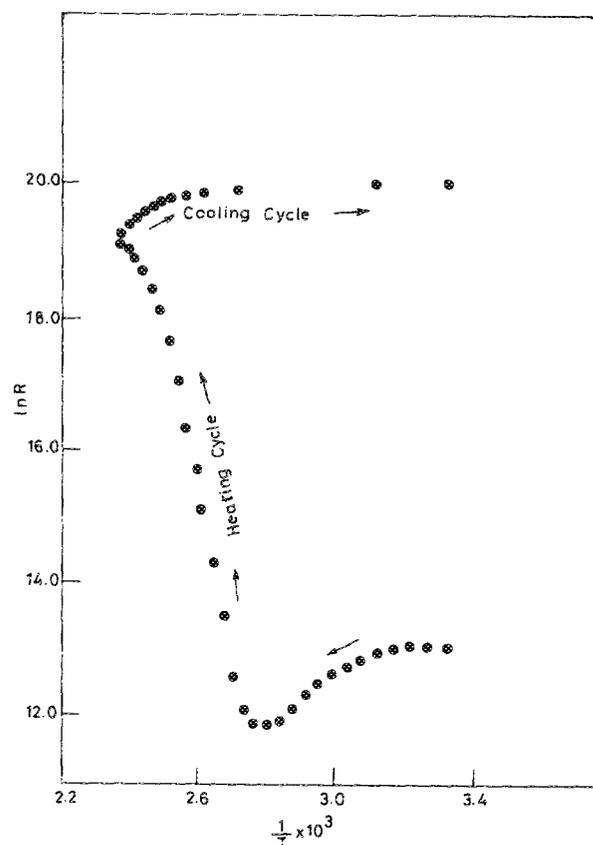


FIG. 3. $\ln R$ vs $1/T$ plot for a film of $R_0 = 0.29 \text{ M}\Omega/\square$ at room temperature during heating and cooling cycles.

tance increase is not due to any change in the substrate property, at least in the beginning. It was expected that in this case, free from the kinetic limitations of vacuum deposition, subsurface structure would be readily formed, but even in this case such a structure does not seem to have formed.

To conclude, for Cu-island films deposited on softened substrate, as well as preformed islands on the substrate subsequently softened, a subsurface particulate structure is not formed which would be protected against atmospheric gases and water vapor when exposed to atmosphere by the surrounding polymer. For such a structure to be formed, a higher substrate temperature can be tried. Some other polymer which can withstand high temperature should be used.

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A field-effect quantum-well laser with lateral current injection

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Polarization-dependent gain switching in a field-effect quantum-well laser with lateral current injection is studied. We use the $\mathbf{k}\cdot\mathbf{p}$ method for the optical dipole matrix and take into account the intraband relaxation. Gain switching is achieved by the field effect from a gate terminal in a lateral current injection quantum-well laser structure. It is shown that the peak gain exhibits a red shift and the peak-gain amplitude decreases with an increasing electric field for the TE mode. The TM mode is less affected by the external field.

Quantum-well lasers are of growing interest because of their superior characteristics, such as low threshold current and narrow gain spectrum, compared with those for conventional semiconductor lasers.¹⁻⁴ Recently, an AlGaAs/GaAs lateral current injection quantum-well laser was proposed in which the structure is planar, suitable for integration with other optical devices, and exhibits built-in index guiding and a very low stray capacitance.⁵ The possibility of electric-field-induced photoluminescence or gain switching in a similar structure with a third terminal has been suggested.^{6,7} Field-induced gain switching has an advantage over the conventional method of controlling injection current in that the former method is not limited by the carrier lifetime which limits the switching speed.⁶⁻⁸ Recent experimental results by Takeoka *et al.*⁸ show that a short optical pulse as narrow as 140 ps full width at half maximum is generated by field-induced gain switching in an optically pumped quantum-well laser.

Arakawa *et al.*⁹ showed active Q switching achieved in another coupled section adjacent to the active region of the conventional quantum-well laser through the quantum-confined Stark effect. There is no applied voltage directly across the active region of the quantum-well laser in the structures, and as a result there is no direct control of the intrinsic gain in the active region.

In this paper, we report theoretical results for gain switching in a lateral injection quantum-well laser with a controlling gate similar to that of a field-effect transistor (Fig. 1). We call it a field-effect quantum-well laser because (i) the electrons and holes are injected laterally by the p and n junctions and they conduct parallel to the quantum-well interfaces, and (ii) the gain switching is achieved by an applied voltage at the gate, thus creating an internal electric field perpendicular to the quantum-well interfaces. The re-

gion below the gate can be an insulating $\text{Al}_x\text{Ga}_{1-x}\text{As}$ or AlAs region.⁷ The electric field will push the electron and hole wave functions to opposite sides of the well in the direction perpendicular to the well, therefore decreasing the overlap integral for optical transitions in the laser structure (Fig. 2). Thus, the gain is decreased by the applied perpendicular field. We show a model calculation of the electric-field dependence of the linear gain in a quantum well where carriers are injected parallel to the well. Our analysis is based on the density-matrix formulation with intraband relaxation.^{10,11} We use the $\mathbf{k}\cdot\mathbf{p}$ perturbation method¹² and envelope-function approximation^{11,13} for the optical matrix element and transition energy.

Let us consider the electrons and holes in a quantum well with a well width L in the presence of an applied electric field F along the direction of the well z . We use an infinite-well model to calculate the wave functions when there is an applied electric field. We choose the origin to be at the center of the well. For simplicity, we assume isotropic and parabol-

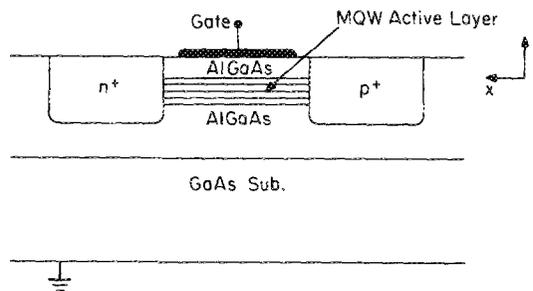


FIG. 1. Structure of a field-effect quantum-well laser with lateral current injection.