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Air-exposure effect on the resistivity of thin bismuth films

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Abstract. A survey of previous studies on vacuum deposited metal films shows that in high frequency measurements, explicit reference to the effect of air-exposure is not made. The present work on bismuth films (*in-situ* and air-exposed) at DC and RF frequencies, carried out mainly to study the air-exposure effect, shows that *in-situ* DC and RF and exposed RF all show nearly the same resistivity for thick continuous films. But air-exposed DC film resistances, when compared to *in-situ* DC resistances, show that the grain boundary reflection coefficient, R_g in Mayadas-Shatzkes model changes from 0·2 to 0·6. This is shown to be due to the grain boundary oxidation. The result is substantiated by RF measurements.

Keywords. Resistivity; grain boundary; oxidation; air-exposure; continuous films; discontinuous films.

1. Introduction

The properties of thin film depend upon its microstructure which in turn depends upon conditions of deposition. Further, while metal films are often evaporated at low residual gas pressures ($\sim 10^{-6}$ torr), they also are transported often in air to the measuring apparatus. Due to such exposure of the films to ambient atmosphere, their electrical resistance changes (Anderson 1971).

Till now large number of measurements on thin film resistivities have been done at DC and RF (Chasmer 1948; Hirsh and Bazian 1964; Licznerski 1978; Mayadas and Shatzkes 1970; Joglekar 1974; Morris 1976). But it should be pointed out that no explicit reference is made in many of the papers to the air-exposure effect, though apparently most of the RF measurements are carried out mainly in normal atmosphere.

The present work was carried out mainly to study this air-exposure effect on the DC and RF properties of bismuth films (particularly for continuous films), deposited at moderate ($\approx 10^{-5}$ torr) vacuum.

2. Experimental

Thin films of bismuth (99·999%) were obtained by vacuum deposition at about 10^{-5} torr on glass substrates at room temperature. The deposition rate was 10 Å–15 Å/sec. The thickness was measured by gravimetric method. For DC and RF resistance measurements, thick aluminium electrodes ($\approx$ 2000 Å), were deposited on the substrate ends. DC resistances, *in-situ* and air-exposed, were measured using a Philips VTVM. The resistance of films, which remained practically constant in vacuum, when exposed to normal atmosphere showed a fast change within 10-20 sec and stabilized after about 2 hr. This resistance of films exposed to atmosphere was measured when the equilibrium value was reached after leaking the system. RF resistances, *in-situ* and air-exposed, were measured using a Marconi Q-meter in the frequency range from 70 kHz to 50 MHz. The electrical connections for *in-situ* measurements were taken out from vacuum system through highly insulated, low capacitance vacuum electrodes. DC and RF resistances were measured at room temperature, the film thickness range being from $\lesssim 100$ Å to 2000 Å measured with the accuracy of $\pm$ 30 Å.

3. Results

The thickness dependence of the relative resistivity (ρ_f/ρ_0) of bismuth films at DC as well as RF frequencies measured both *in-situ* and in normal atmosphere, are shown in figure 1. Some theoretical curves, calculated from Fuchs–Sondheimer (FS) (Sondheimer 1952) and Mayadas–Shatzkes (MS) (Mayadas and Shatzkes 1970) theories, are also presented in figure 1 for comparison. The observed variation of resistance with frequency for continuous films (3 thicknesses) is shown in figure 2. Figure 3 shows

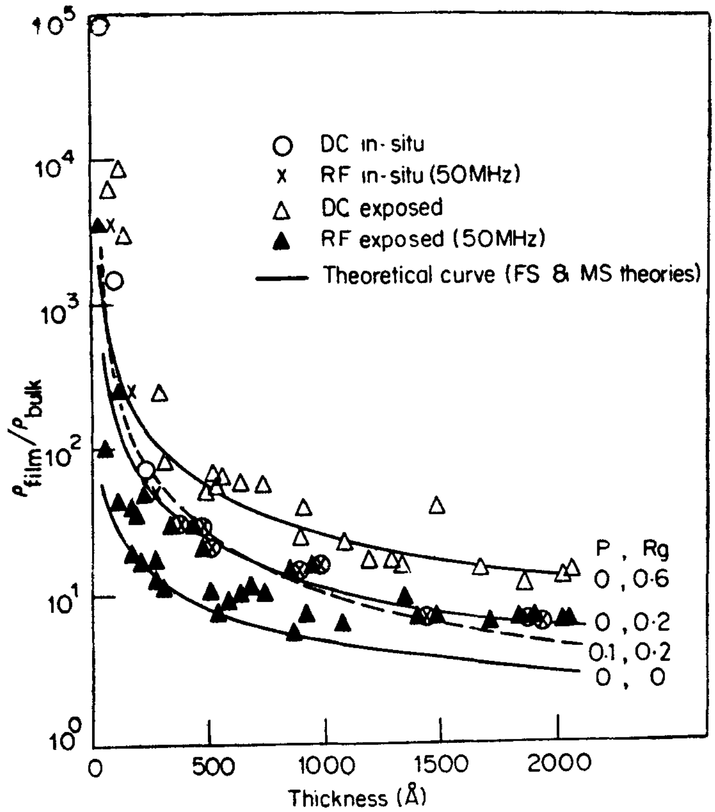

Figure 1. Ratio of film resistivity to bulk resistivity ($\rho_0 = 1{\cdot}20 \times 10^{-6}$ mhos-metre) versus thickness under various conditions. RF *in-situ* and RF exposed are co-incident but exposed points (▲) are shown by the side for convenience.

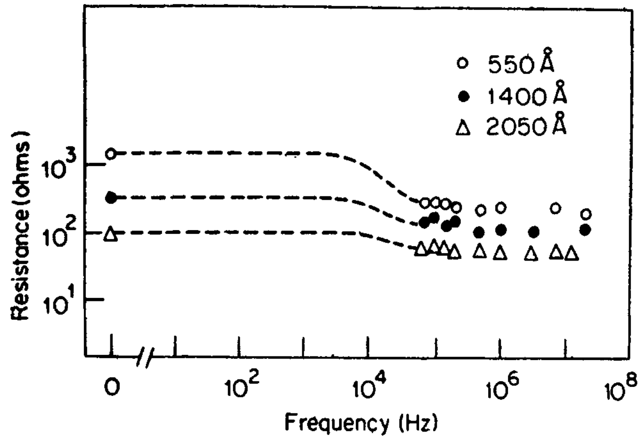

Figure 2. Resistance frequency behaviour of exposed continuous films (t >350 Å) for different thicknesses.

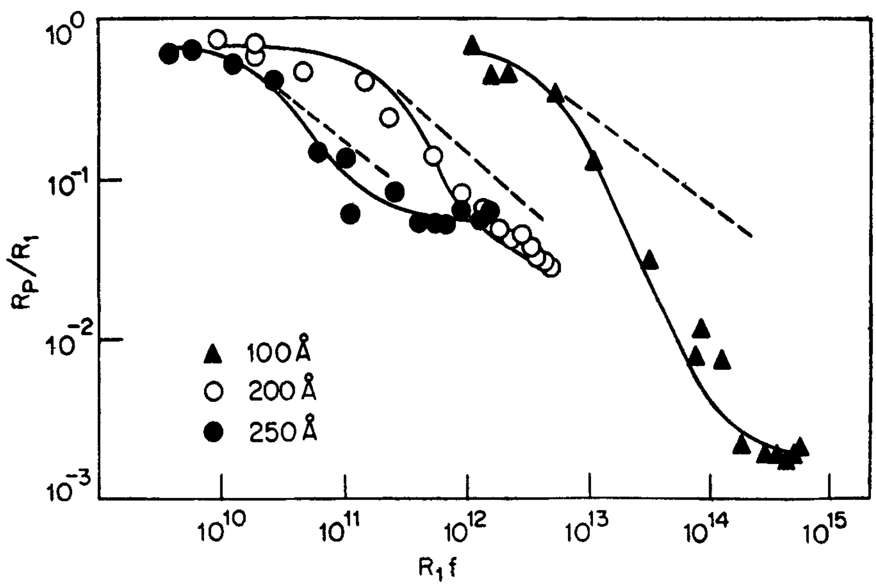

Figure 3. Resistance frequency behaviour (normalized following Humphrey) of exposed discontinuous films (t < 350 Å) for different thicknesses.

the frequency variation for discontinuous films (3 thicknesses), but normalized following Humphrey *et al* (1953).

4. Discussion on air-exposure effect

The *in-situ* and the normal atmosphere DC measurements show that below about 350 Å, the resistivity variation is sharper than that above 350 Å, as would be expected for discontinuous and continuous films respectively (Joglekar 1974b,c), the exposed values being higher. The deviation of observed resistivity for these unannealed polycrystalline films from that of bulk, attributed to the thickness and grain size variation, is estimated theoretically using Fuchs–Sondheimer (Sondheimer 1952) and Mayadas–Shatzkes (Mayadas and Shatzkes 1970) theories. It can be seen from figure 1 that on the average, for continuous films, the observed *in-situ* DC resistivity data fits best with the curve, where $p = 0$, $R_g = 0{\cdot}2$ and exposed film DC resistivity data averages with $p = 0$, $R_g = 0{\cdot}6$ curve, where p is the specularity parameter in FS theory and R_g is the grain boundary reflection coefficient in MS theory. The reported (Joglekar 1974b) p and R_g values for unannealed bismuth films are nearly same as ours and even for annealed films the reported (Kawazu 1976) R_g value is 0·12 at about room temperature. However, the reported p values are of the order of 0·6 (Kawazu 1976) and 0·9 (Sen and Pal 1975). This is expected as the difference between annealed and unannealed films (Maissel and Glang 1971; Joglekar 1974c). The initial value of R_g (=0·2) in the present work may be inclusive of small exposure effect due to medium vacuum that we use ($\approx 10^{-5}$ torr); however, major change in R_g value from 0·2 to 0·6 is being discussed below. For discontinuous films because of their island structure, both FS and MS theories do not apply.

4.1 *Discontinuous films—*DC *and* RF *measurements*

The DC resistance of discontinuous films ($t < 350$ Å, figure 1) increases on exposure to air as for continuous films. But at RF as against the constant resistance of continuous films ($t \geqslant 350$ Å, figure 2), these films show a large variation in resistance with frequency (figure 3). The resistance of the films at low frequency is nearly equal to its DC (exposed) film resistance. It decreases with frequency and tends to reach an approximately constant value at frequency of the order of few MHz. The observed variation of resistance with frequency of discontinuous films fits properly with the model given by Chasmar (1948). The values of capacitances determined from resistance-frequency behaviour are of the order of picofarads (table 1), which are nearly same as those reported by Joglekar 1974b,c; for *in-situ* measurements on bismuth and other films (Deshpande and Crowell 1971; Drumheller 1957; Joglekar 1974; Licznerski 1978).

Table 1. Resistance capacitance parameters (discontinuous films).

Thickness (Å)	Substance	R_{DC} Ohms	R_1 Shunt Ohms	R_2 Series Ohms	C_1 Inter-island picofarads	C_D Distributed picofarads
100	Bi*	$1{\cdot}14 \times 10^7$	$1{\cdot}14 \times 10^7$	$3{\cdot}60 \times 10^4$	$0{\cdot}5 \pm 0{\cdot}1$	$1{\cdot}5 \pm 0{\cdot}2$
140	Bi**	$2{\cdot}00 \times 10^6$	$1{\cdot}90 \times 10^6$	$4{\cdot}00 \times 10^4$	$0{\cdot}5 \pm 0{\cdot}2$	$1{\cdot}2 \pm 0{\cdot}2$
150	Bi*	$4{\cdot}50 \times 10^5$	$4{\cdot}40 \times 10^5$	$6{\cdot}70 \times 10^3$	$1{\cdot}5 \pm 0{\cdot}3$	$2{\cdot}0 \pm 0{\cdot}5$
200	Bi*	$1{\cdot}24 \times 10^5$	$1{\cdot}19 \times 10^5$	$5{\cdot}28 \times 10^3$	$3{\cdot}0 \pm 0{\cdot}2$	$8{\cdot}0 \pm 1{\cdot}5$
	Bi**	$1{\cdot}30 \times 10^5$	$1{\cdot}20 \times 10^5$	$4{\cdot}8 \times 10^3$	$2{\cdot}7 \pm 0{\cdot}5$	$5{\cdot}0 \pm 1{\cdot}0$
250	Bi*	$3{\cdot}50 \times 10^4$	$3{\cdot}20 \times 10^4$	$3{\cdot}00 \times 10^3$	$20{\cdot}0 \pm 3{\cdot}0$	$50{\cdot}0 \pm 5{\cdot}0$
270	Bi**	$1{\cdot}40 \times 10^4$	$1{\cdot}20 \times 10^4$	$1{\cdot}50 \times 10^3$	$35{\cdot}0 \pm 5{\cdot}0$	$110{\cdot}0 \pm 10{\cdot}0$
—	Mo+	$4{\cdot}75 \times 10^6$	$3{\cdot}71 \times 10^6$	$1{\cdot}06 \times 10^6$	0·21	...
—	Cr++	—	$1{\cdot}11 \times 10^{10}$	$3{\cdot}85 \times 10^5$	2·0	...
—	Cr++	—	$1{\cdot}13 \times 10^{11}$	$1{\cdot}11 \times 10^6$	0·24	...

*Present data

**data from Joglekar (1974 a, c)

+data from Deshpande and Crowell (1971)

++data from Licznerski (1978)

4.2 *Continuous films —DC measurements*

An increase in the DC resistivities of the continuous films on air-exposure can be attributed to the adsorption of ambient gases and the oxidation of bismuth. The increase in the film resistance of continuous films (giving an R_g change from 0·2 to 0·6) cannot be explained on the basis of the simple oxidation model (Anderson 1971) based on the replacement of a conductive bismuth surface layer by an insulating oxide film. For example, in case of a film 2050 Å thick a bismuth layer of 586 Å thickness should get converted into an oxide (Bi_2O_3) layer, to give the observed typical resistance change of about 30 ohms on exposure. The ratio of molar volumes of Bi_2O_3 to Bi is 1·17. The oxidation rate at 200 °C is about 16 Å/min. (Pande 1976). At room temperature, which was used in the present work, the oxidation rate will be smaller still (a few Å/min.) and after forming an oxide layer at the top of the film the rate will be reduced further. Hence as suggested by Basseches (1961) and Maissel (1962), the resistance change on exposure must be attributed to oxide layers in series with the metal crystallites. Consequently very small amount of oxide can exert a much greater influence on the film resistance.

As a consequence of grain boundary oxidation, the grain boundary reflection coefficient may change. The R_g can be expressed (Mayadas and Shatzkes 1970) in terms of the strength (S_g) of a potential barrier which in turn is the product of potential height V_g and barrier width W_g. Thus the change in R_g may be due to the change in V_g and/or change in W_g. The observed increase in R_g value from 0·2 to 0·6 indicates that the grain boundary potential has changed from 0·23 to 0·57 eV for fermi velocity $v_f = 10^8$ cm/sec and $W_g = 10$ Å. Attributing the change in S_g to W_g only (*i.e.* assuming grain boundary potential to be the same as that before the exposure *i.e.* 0·23 eV with W_g equal to 10 Å) (Drumheller 1964), one gets W_g change from 10 Å to 25 Å *i.e.* each grain has reduced in width by just 7 Å on each side. As normally this oxidation is seen to take about an hour, this value of 7 Å appears to be a fair estimate, if compared to the above mentioned value of oxidation rate of 16 Å/min at 200 °C, keeping in view the fact that oxidation of the sides of grain may be slower than that at the top.

4.3 *Continuous films—RF measurements*

The second way to verify the above result, about grain boundary oxidation, is by using the high frequency characteristics of films following Maissel (1962). Referring to figure 1 or 2 it is observed that (i) DC *in-situ* and RF *in-situ* resistances of films are nearly the same, particularly for continuous films (which are also practically the same at microwave x-band frequency)* (ii) there is an increase in DC resistivities of continuous films when exposed to atmosphere but (iii) there is no measurable change in RF resistivities of films (figure 1) when exposed to atmosphere. (As seen from individual film readings there is some variability from film to film in all DC and RF measurements. But it can be expected to be due to deposition method and corresponding crystallite size variation.) It is clear that an oxidised grain boundary having metal on either side of the oxide layer, constitutes a capacitor. The nearly constant resisti-

*These micro-wave observations are being reported in a separate communication.

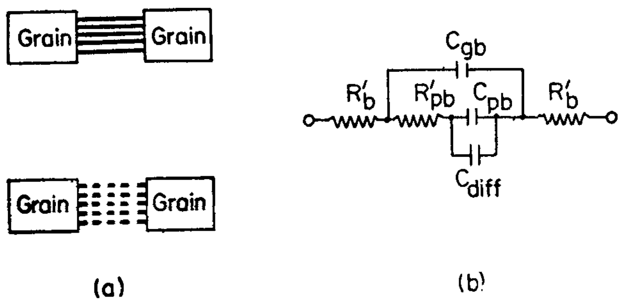

Figure 4. Bridge path model. R'_b—grain resistance, R'_{pb}—fraction of bridge path resistance, C_{gb}—grain boundary capacitance, C_{pb}—bridge path capacitance, $C_{diff.}$—diffusion capacitance.

vity of the films, thicker than about 1000 Å, in the frequency range from 70 kHz to 50 MHz (figure 2) indicates the existence of high intergrain capacitances.

4.4 *Concluding remarks*

Our observation about RF resistance, which does not change on exposure, indicates that as far as electrical equivalent circuit is concerned the grain boundaries are not effective *i.e.* are shorted somehow giving the same resistance in shorting path for both RF *in-situ* as well as exposed. Further because the DC *in-situ* and RF resistivities are same, it means that for DC *in-situ* films also the grain boundaries do 'short' the grains practically in same way as for RF, which get 'opened' for DC only on exposure. The openings have no effect on RF. Considering these facts, we tentatively propose, on the lines of discontinuous film models, a qualitative electrical equivalent model shown in figure 4. The grains are shorted by some metallic contacts or bridge paths of resistance R_{pb}. On exposure these bridge paths break at various points and DC resistance increases. However, for RF these breaks being very small; may represent capacitive short with possibly somewhat higher C_{pb} (compared to that required for discontinuous films) and hence no change in RF resistance on exposure. Even though this model explains results of DC exposed—unexposed versus RF results, it is difficult to see how it meets the exact physical situation. It may be remarked that, at lower frequencies, the discontinuous films behave similar to continuous films, in the sense that DC and RF resistances are same for a film.

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