

# Electrical resistivity of polycrystalline vanadium films

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The electrical resistivity of polycrystalline vanadium films (20 to 400 nm thick) deposited on to amorphous and crystalline substrates heated to 473 K during deposition was studied. The data were interpreted in terms of the classical size effect for thick films. The mean free path,  $l_0$ , the average resistivity,  $\rho_0$ , and the density of conduction electrons,  $N$ , were calculated. These values are compared with those found in earlier works.

## 1. Introduction

It is well known that thin metal films have higher resistivities than the bulk metal. This is a result of electrical external and internal size effects as well as a result of lattice imperfections which are more pronounced in thin films. Ramesh *et al.* [1] studied the electrical conductivity and Hall effect in thin vanadium films which were prepared by evaporating the metal at room temperature and at a pressure of  $10^{-4}$  Pa on to glass. On heating the films to higher temperatures, there was an irreversible rise in resistance, an increase in the Hall coefficient, and a decrease in Hall mobility, presumably due to the fact that a substantial part of the vanadium was oxidized. The thickness dependence of the temperature coefficient of resistance in vanadium films has been determined over the range 6 to 90 nm [2].

Reale [3] studied the size effects for vanadium thin films. He determined the charge-transport parameters for metals with cubic symmetry. The results in this paper are consistent with those deduced for the elements of the vanadium and chromium families [4] from considerations involving analysis of the optical behaviour of thin films. The carrier concentrations are in reasonable agreement with the generally accepted electronic structure of transition metals [5], but depart appreciably from a recent estimate [6] of the numbers of valence electrons contained in the s and p bands.

The electrical size effect of polycrystalline vanadium films evaporated on to glass substrates at room temperature was studied [7]. It has been shown that grain-boundary scattering and additional defect scattering are considerable and they cannot be neglected. On the basis of the electrical size effect, the electron mean free path for the temperature range 293 to 575 K has been found to vary from  $12.3 \times 10^{-10}$  to  $7.7 \times 10^{-10}$  m.

The electrical resistivity of vanadium was measured in the temperature range 6 to 327 K [8], and was analysed following the theories of Bloch-Grüneisen and Wilson. The low-temperature (6 to 12 K) data were analysed for the existence of a quadratic temperature dependence with coefficients of  $370 \text{ f}\Omega\text{m K}^{-2}$ .

## 2. Experimental procedure

Pure vanadium (99.999%) was deposited at a rate of

about  $3 \text{ nm sec}^{-1}$  from a tungsten boat on to glass slides and on to freshly cleaved mica and rock salt substrates held at 473 K during the evaporation. The substrate was mounted on a holder whose temperature could be varied from 300 to 473 K. Thick silver films were deposited at the substrate ends, prior to vanadium deposition and served as contact electrodes. The evaporation processes were carried out in a vacuum  $\sim 10^{-4}$  Pa and the resistivity of the films as a function of temperature was measured *in situ*. After condensation, the films were kept in the vacuum conditions used for their preparation and cooled to room temperature slowly enough to minimize the structural alteration arising from differential thermal expansion between metal and substrates. The temperature was measured using a nickel-nickel/chromium thermocouple. The film thickness was determined by multiple beam interferometry [9]. The vanadium films deposited on thin carbon films were ready as-prepared for examination by electron microscopy. However, the films deposited on rock salt substrates were removed from the substrate by immersion in distilled water and the floating deposits were supported on fine mesh grids. An EM 10-Zeiss electron microscope was employed for microstructural examination. Resistivity was measured using the potentiometric technique.

## 3. Results and discussion

Several investigators [10-13] have pointed out that the electron mean free path in thin films may be restricted by the film thickness and, consequently, the electrical properties of thin films should differ from those of the bulk, and should in some way depend on the film thickness.

The electrical resistivity of the continuous layers of vanadium deposited on different substrates heated at 473 K *in situ*, were fitted to the Fuchs theory [11] which gives an expression for the size-effect dependence of film resistivity,  $\rho$ , as

$$\rho/\rho_0 = \left\{ 1 - \frac{3(1-P)}{2\gamma} \int_1^\infty (a^{-3} - a^{-5}) \times \frac{[1 - \exp(-\gamma a)]}{[1 - P \exp(-\gamma a)]} da \right\}^{-1} = \phi(p, \gamma) \quad (1)$$

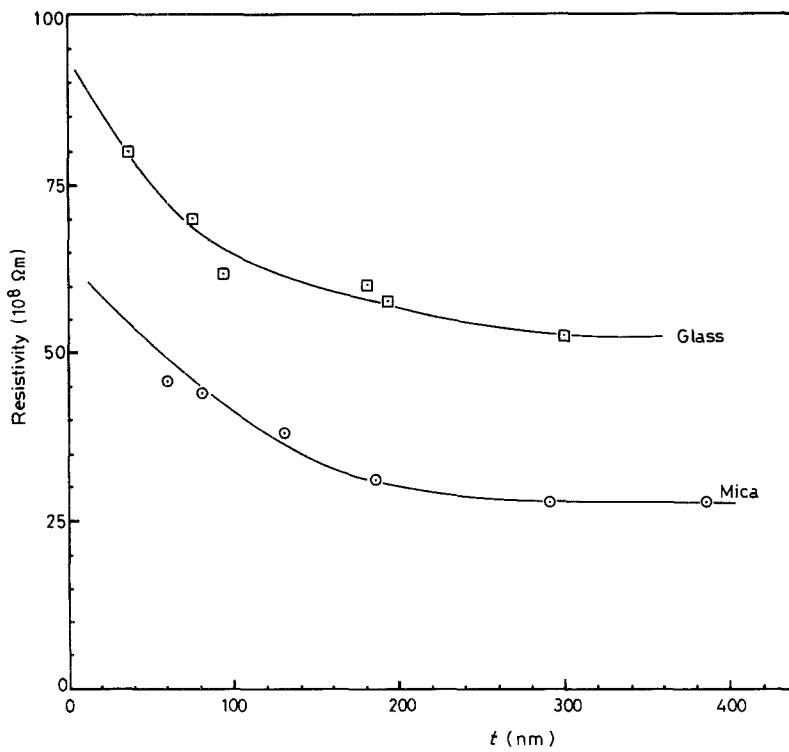


Figure 1 Resistivity against thickness plot for vanadium films deposited on glass and mica substrates heated to 473 K during evaporation.

where  $\varrho_0$  is the bulk resistivity,  $\gamma$  is the ratio of the film thickness,  $t$ , to the electron mean free path,  $l_0$ ,  $a$  is equal to  $1/\cos \theta$  (the electron mean free path makes an angle  $\theta$  with the normal to the film), and  $P$  is the coefficient of specular reflection of electrons from the film boundaries ( $0 \leq P \leq 1$ ). A convenient form of the above expression for the resistivity has been given by Chambers [14] and by Sondheimer [15]. The limiting form of resistivity is given by

$$\varrho/\varrho_0 = 1 + k \frac{(1 - P)}{\gamma}, \quad \gamma > 1 \quad (2)$$

Mayadas and Shatzkes [16] and Wissman [17] studied the dependence of resistivity on thickness-dependent scattering at the crystalline boundaries. They obtained the following expression for total resistivity

$$\varrho = \varrho_0 \left\{ 1 + [k(1 - P) + k'] \frac{l_0}{t} \right\} \quad (3)$$

where  $k$  is a constant equal to  $3/8$  in the Fuchs-Sondheimer theory,  $k'$  is a factor which takes into account boundary scattering,  $l_0$  and  $\varrho_0$  are the mean free path and resistivity of a film of infinite thickness, respectively.

Borodziuk *et al.* [7] have added another factor,  $k''$ , to Equation 3. This factor takes into account the scattering of electrons on additional defects and adsorbed atoms. Accordingly, the film resistivity was then given by

$$\varrho = \varrho_0 \left\{ 1 + [k(1 - P) + k' + k''] \frac{l_0}{t} \right\} \quad (4)$$

The mean free path,  $l_0$ , and the resistivity,  $\varrho_0$ , are related to the effective density of the charge carriers,  $N$ , by the relation

$$l_0 = (h/2e^2\varrho_0)(3/\pi N^2)^{1/3} \quad (5)$$

where  $h$  is Planck's constant and  $e$  is the electronic charge.

Fig. 1 shows the thickness dependence of the electrical resistivity at 300 K for vanadium films grown on glass and mica substrates. The decrease in resistivity is high for small variations in thickness less than 10 nm. When atoms are condensed in vacuum from the vapour phase, they temporarily retain their mobility on the substrate surface and are captured by crystallization centres such as cleavage steps, points of emergence of dislocations on the surface, point defects, etc. Isolated island nuclei grow at this stage. Naturally, the resistivity of such films is effectively governed by the resistivity of the dielectric substrate. When the dimensions of the crystallites increase sufficiently to form bridges between isolated islands, the resistivity falls sharply. As the film grows thicker, the variation in resistivity with increasing thickness is small compared with the values for the discontinuous films [18]. However, even at larger thicknesses (400 nm) the resistivity is higher than the bulk metal [19] which indicates the presence of structural imperfections in the films [20]. This is normal for evaporated films, especially those of high melting temperatures which increase their ability to absorb gases. Furthermore, they grow in separate islands and still retain this behaviour even at higher thicknesses. It is clear from the figure, that the reduction in the resistivity of continuous films deposited on mica with respect to those deposited on glass is attributed to the good ordering in the films grown on crystalline substrates, especially at high substrate temperature. Similar results have been found earlier [18, 21] and have been confirmed by electron microscopy.

Representative transmission electron micrographs showed that the films, less than 40 nm thick, deposited on either glass or mica substrates are discontinuous having an island structure (Fig. 2a, b) whereas thicker films are continuous.

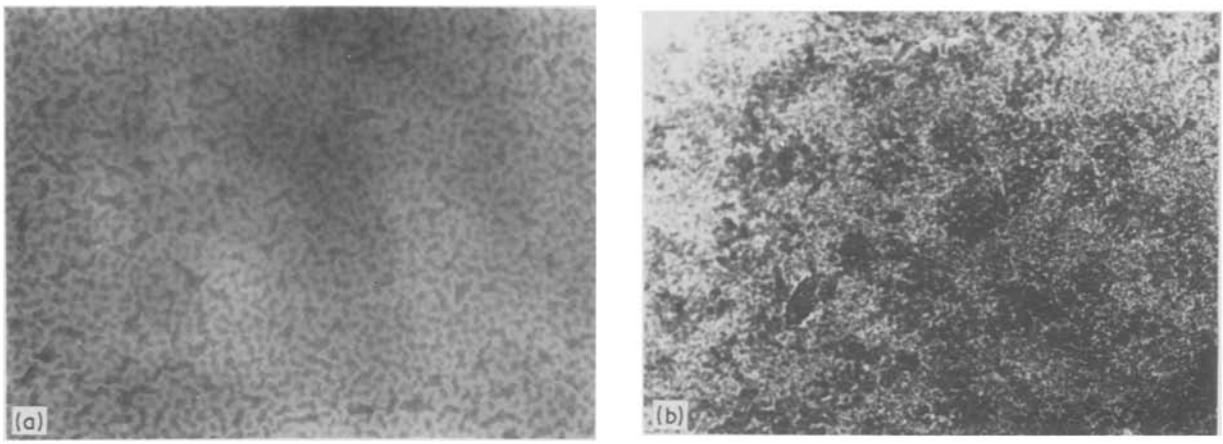


Figure 2 (a, b) Transmission electron micrographs of vanadium film deposits on carbon and rock salt substrates, respectively. (a) 35 nm thick, (b) 40 nm thick.  $\times 7200$ .

The experimental data were fitted by the least squares method and yielded a linear relation between  $\rho t$  and  $t$  (Fig. 3). The slope yields a value of  $35 \times 10^{-8}$  and  $50 \times 10^{-8} \Omega\text{m}$  for  $\rho_0$  for mica and glass substrates, respectively. The intercept can be interpreted in two different ways. Firstly, according to Equation 2 with  $P = 0$  the intercept is equal to  $3/8 \rho_0 l_0$ . This yields values of  $75 \times 10^{-10}$  and  $50 \times 10^{-10}$  m for  $l_0$  using mica and glass substrates, respectively. These values are much smaller than the values of  $600 \times 10^{-10}$  and  $1000 \times 10^{-10}$  m reported by Ramesh *et al.* [1]. On the other hand, the value of  $l_0 = 50 \times 10^{-10}$  m is in good agreement with the value of  $47 \times 10^{-10}$  m which is reported by Reale [3]. The value for  $l_0$  of  $75 \times 10^{-10}$  m is somewhat bigger, but the value of  $\rho_0 l_0$  of  $26.25 \times 10^{-16} \Omega\text{m}^2$  for films on mica is very close to the value of  $\rho_0 l_0$  ( $25 \times 10^{-16} \Omega\text{m}^2$ ) for films grown on glass under the same conditions. The values of  $\rho_0 l_0$  are used to estimate the effective number of electrons according

to Equation 5. This yields a value of 0.2 electron/atom for vanadium films deposited both on heated mica and glass. This value is less than the value of 0.48 electron/atom reported by Reale [3]. Secondly, our values for  $\rho_0$  and  $l_0$  are greater than the values reported by Radebanck [22] and Borodziuk *et al.* [7].

In all the relations mentioned, a plot of  $\rho t$  against  $t$  should be linear and the slope equal to  $\rho_0$  the resistivity of the film of infinite thickness. From the intercept and the value of  $\rho_0$  one may be able to estimate the value of  $[k(1 - p) + k' + k'']$  times the unknown value of  $\rho_0 l_0$ . Undoubtedly the value of  $\rho_0$  ought to be the slope of our linear relation between  $\rho t$  and  $t$ , but the rest of the quantities are questionable. Borodziuk *et al.* [7] considered the value of  $\rho_0 l_0$  given by Radebanck *et al.* [22] of  $3.5 \times 10^{-16} \Omega\text{m}^2$  and estimated the value  $11.3 \times 10^{-10}$  m for  $l_0$  at room temperature. Using this value for  $\rho_0 l_0$ , they estimated the value as 18.6 for  $[k(1 - P) + k' + k'']$ . If we consider their values of

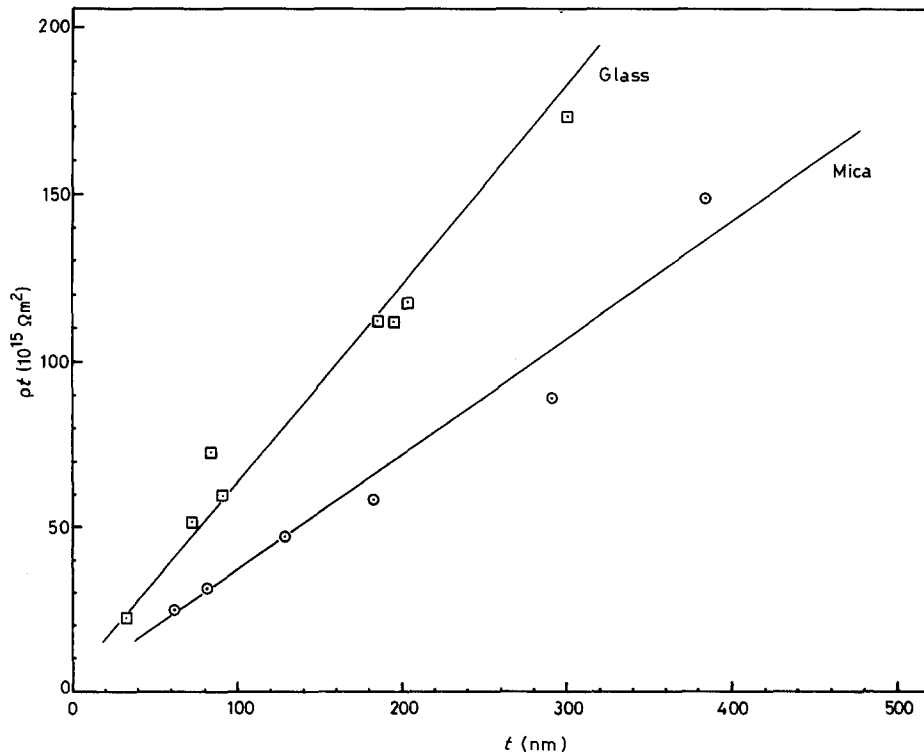


Figure 3  $\rho t$  against  $t$  plot for vanadium films deposited on glass and mica substrates.

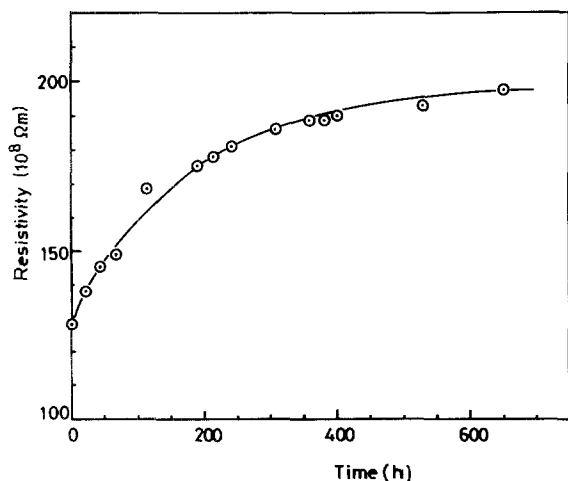


Figure 4 Resistivity against time plot for vanadium films deposited on glass substrate.

$31.7 \times 10^{-8} \Omega\text{m}$  and  $11.3 \times 10^{-10} \text{m}$  for  $\rho_0$  and  $l_0$ , respectively, four electrons/atom have to be considered. This value is much greater than the effective number 0.6 electrons/atom which is known for the transition metals. In the light of these results we used the relation given by Reale [3] to estimate a value of  $13.9 \times 10^{-16} \Omega\text{m}^2$  corresponding to the value of 0.48 electrons/atom given there. Inserting these values in our results we obtain a value of  $27.75 \times 10^{-10} \text{m}$  for  $l_0$ . Accordingly the value of 0.72 stands for  $[k(1 - P) + k' + k'']$ , keeping in mind that our specimens were evaporated on heated substrates during preparation, so the probability for adsorbed atoms is weak and the temperature is not so high for the grains to have any considerable role in the size effect study. In the light of these estimations it may be possible to assign the value of 0.72 for  $k$  instead of the value of  $3/8$  assigned earlier by Fuchs and Sondheimer. In fact, according to Wedler *et al.* [23] a value greater than  $3/8$  had already been assigned for  $k$ .

Thin metal films deposited from the vapour are in a state of strain not associated with the bulk metal which crystallizes from the melt. Accordingly, the metal films are thermodynamically unstable, and their physical characteristics usually change with time and heating. Fig. 4 shows the variation of resistivity with time for a continuous vanadium film deposited on a cool glass.

A sharp increase in resistance with time occurred for up to about 200 h after film preparation indicating

a rapid oxidation reaction. At longer times the rate of resistance increase is much smaller and the resistance tended to a constant value. This behaviour is attributed to the growth of a continuous vanadium oxide film during the early stages. After ageing for a long time the rate of oxide growth decreases and the continuous oxide film acts as a passivating layer. The growth is then controlled by the porosity and kinetics of the ion diffusion, either vanadium or oxygen, through the continuous oxide layers.

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