Structure and optical properties of evaporated films of vanadium

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In the present work, the interpretation of the structure, nucleation and growth of Vanadium films will be studied. Film structure was inferred from transmission electron diffraction and microscopy of vanadium films evaporated simultaneously onto freshly cleaved rocksalt and carbon substrate. The investigated films were from about 10 to 80 nm thick, and the rate of the deposition was fixed at 3 nm sec^{-1} throughout this work. The optical constants were determined for vanadium from transmission measurements on vacuum-evaporated polycrystalline thin films at room temperature in the infrared range. Transmission measurements were made on films in the thickness range 100 to 150 nm.

1. Introduction

Thin films of the refractory transition metals body-centre cubic (b c c) chromium (Cr), tungsten (W), vanadium (V), and tantalum (Ta) are used in many technical applications. Most of these applications depend on the atomic and electronic structure of the films, in some, the optical properties of the film are themselves of direct concern [1]. This paper describes the structure and the real (ε_1) and imaginary (ε_2) parts of the complex dielectric constant of V thin films deposited on different substrates at room temperature and with an evaporation rate of 3 nm sec^{-1}. The dependence of the shape and orientation of the crystallites on the substrate was examined.

The optical properties of thin metallic films as a function of their structure has been studied by many authors. Previous works are summarized in the survey articles [2–6]. Self-consistent band calculations are carried out for vanadium. The modified tight-binding method and the orthogonalized-plane-wave method are made use of, for the wave functions of *d* and *s*-electrons, respectively. The crystal potential and wave functions are determined self-consistently by an iteration method. The band structures, fermi surfaces, and density of states curves are obtained for vanadium and compared with previously reported results [7].

The energy loss of electrons in thin evaporated films of the metals V and Cr of the first transition series has been determined in transmission for the spectral region 3–80 eV.

The complexity of the spectrum increases along the series as the 3*d* shell is completed. In vanadium and chromium the main peak (22–25 eV) in the spectrum is attributed to a collective excitation (4*s* + 3*d* electrons) [8]. The characteristic energy losses observed on vanadium are interpreted as due to free electron bulk and surface plasmons and/or combinations of both. Characteristic ionization losses confirm the ODS peaks observed in the vanadium valence band and indicate high transition probabilities for the top and bottom of this band [9].

Bulk vanadium specimens have a b c c lattice at room temperature [10]. The V films deposited in air and vacuum-cleaved NaCl crystals were partially oriented and composed of b c c lattice crystallites. The preferred orientation with respect to the NaCl was such that $(0\,0\,1)\,[1\,0\,0]_V//(0\,0\,1)\,[1\,1\,0]_{NaCl}$. Single crystal vanadium films were obtained on the LiF layers, all the crystallites being oriented with respect to the LiF according to the same scheme [11].

The structure and optical properties of evaporated films of the Cr and V group metals were studied [1, 12]. Vanadium films rapidly evaporated onto room-temperature substrates have the reflectance of bulk crystalline material. On liquid nitrogen temperature substrates, vanadium have normal b c c crystal structure but with small flate-plate grains [1]. Saito *et al.* [13] studied the crystal structure and habit of fine metal particles formed by gas-evaporation technique. Vanadium particles grown in all zones have the ordinary b c c structure. The external shape, which has been reported as a complex polyhedron [14], can be determined as a rhombic dodecahedron truncated by six (1 0 0) faces [13].

Finally, optical absorption of vanadium thin films has been determined from 0.32 to 5.5 eV from reflectance and transmittance data. The films have been deposited in ultra high vacuum and the measurements have been realised *in situ*. Between 1 to 5.5 eV, the absorption band explained by direct interband transitions deduced from theoretical bands calculated by Yasui *et al.* [7]. But from 0.32 to 1 eV, the observed absorption is principally due to intraband transitions.

2. Experimental technique

High purity vanadium (99.999%) was employed for the deposition of thin films in vacuum $\sim 10^{-4}$ Pa by evaporation from a tungsten boat onto an amorphous carbon and freshly cleaved surface of rock-salt at room temperature. The rate of deposition was estimated interferometrically to about 3 nm sec^{-1}. Afterwards, the deposited vanadium films on thin carbon

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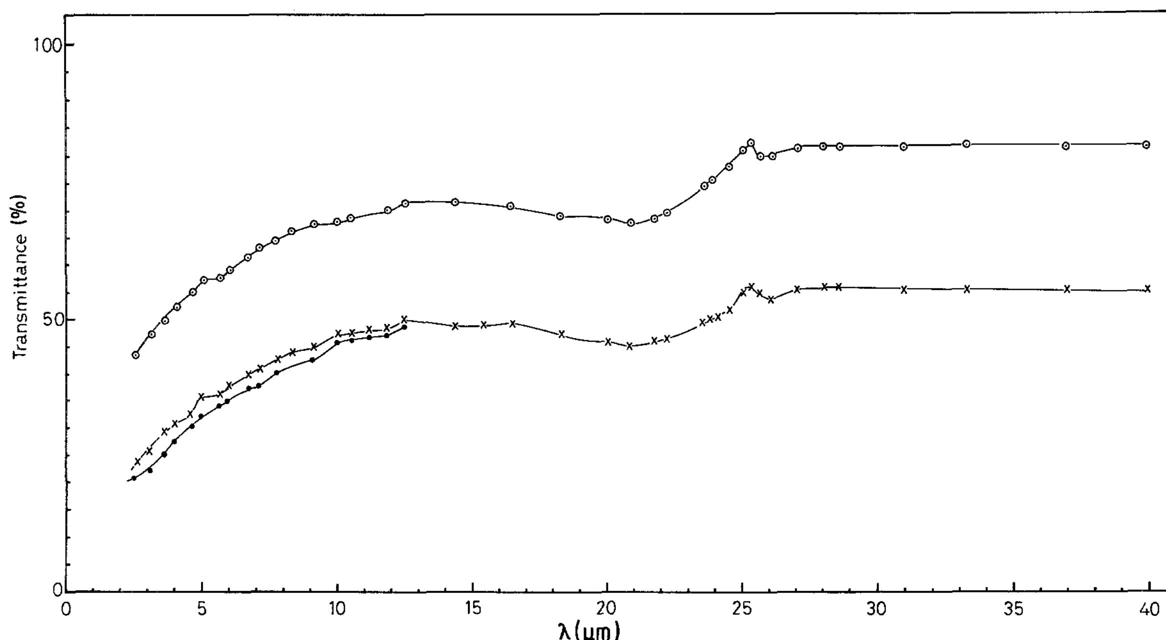


Figure 1 Transmittance against wavelength for vanadium films of different thicknesses (●) $d = 150$ nm, (x) $d = 140$ nm, (⊙) $d = 102$ nm.

films were ready for the examination by electron microscopy. On the other hand, the deposited films on rocksalt substrates were then removed from the substrate by immersion in distilled water and the floating deposits supported on fine mesh grids. The film thickness was measured by Tolansky interference method [15]. The films were investigated by means of a transmission electron microscope (EM 10-zeiss). The optical transmittance in the infrared range was measured for films deposited onto KBr discs using a double beam spectrophotometer (IR 4220 Beckman).

3. Results and discussion

The optical constants of the films were determined from the transmission curves obtained on the (IR 4220 Beckman) spectrophotometer in the range from 2 to 40 μm. Fig. 1 shows the transmitted scattered light against wavelength for different thickness vanadium films. The transmittance shows a minimum near 20.83 μm and a maximum near 25.32 μm, moreover, the transmittance decreases and increases gradually as the film thickness and wavelength increases respectively. Earlier measurements of the infrared transmission of metal films have shown that transmission increases with increasing wavelength. This phenomenon has been noted by other workers [16].

The optical constants: the extinction coefficient (k) and the refractive index (n) can be calculated, for thick absorbing film satisfying the condition $4\pi kd > \lambda$, using, the equation of Tubbs [17], Brattain and Briggs [18] for the transmitted intensity:

$$T = \frac{16n_1(n^2 + k^2)}{[(n + 1)^2 + k^2]\,[(n_1 + n)^2 + k^2]} \times \exp\left(-\frac{4\pi kd}{\lambda}\right) \quad (1)$$

where T is the transmitted intensity, d is the film thickness and n_1 is the refractive index of the substrate. The extinction coefficient (k) and the refractive index (n) can be estimated from the pre-exponential factor using the experimental values of T, d, n_1 and k.

The variation of the calculated values of the optical constants (n) and (k) with wavelength is shown in Fig. 2. The extinction coefficient (k) and the refractive index (n) increases with the increase of the thickness.

The optical properties of films are characterized by the refractive index (n) and the extinction coefficient (k). These parameters are combined to give the complex refractive index (m) by the relation $m = n - ik$ where $i = \sqrt{-1}$. The coefficient (n) is related to the magnitude of light absorption and the coefficient (k) is related to the frequency of light absorption. The index (m) is related to the complex dielectric constant ε by the relation

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 = m^2 \quad (2)$$

where ε_1 and ε_2 are the real and the imaginary parts of the dielectric constant, respectively.

The real and imaginary parts of the dielectric constant are related to (n) and (k) by the relations

$$\varepsilon_1 = n^2 - k^2 \quad \varepsilon_2 = 2nk \quad (3)$$

Fig. 3 shows their behaviour as a function of wavelength.

The intraband contribution to the dielectric constants can, therefore, be separated from the interband contribution by determining values for the free-electron optical mass and relaxation time at long wavelengths. The optical mass is determined from the long-wavelength slope of a plot of $-\varepsilon_1$ against λ^2 and then the relaxation time from the slope of a plot ε_2/λ against λ^2. Such a technique fails for vanadium discussed here, since the plots are not linear as required by free-electron theory. Our results agree with the results of Johnson *et al.* [12].

The processes of nucleation and growth of thin films have been of considerable interest in studies of physical properties of materials and in studies of applications of these properties to practical

Figure 2 Spectral behaviour of the real and imaginary parts of the refractive index (⊡) d = 102 nm, (⊙) d = 150 nm.

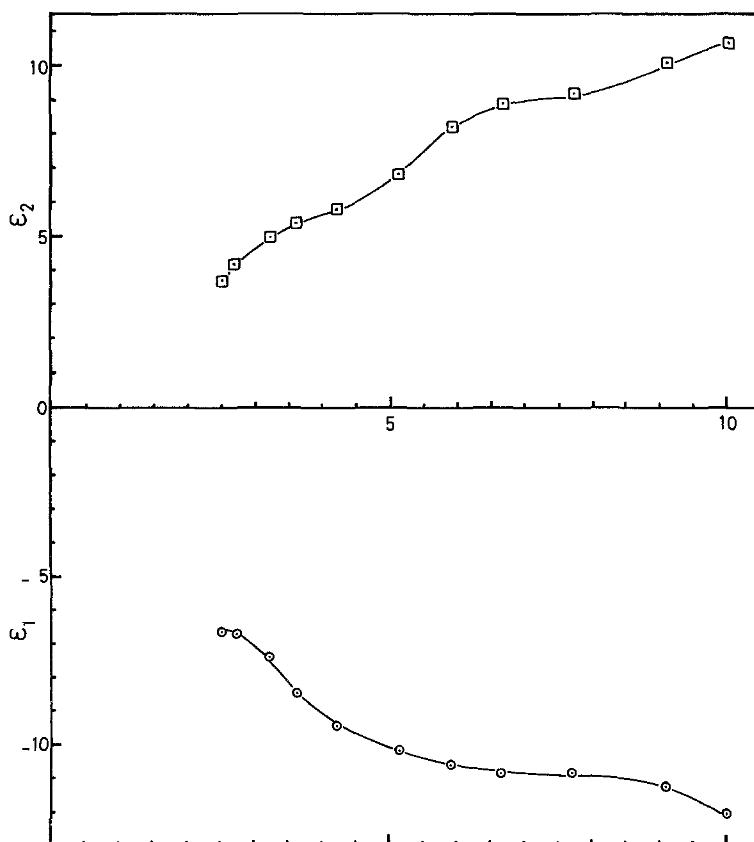


Figure 3 Spectral behaviour of the real and imaginary parts of the dielectric constant, d = 150 nm.

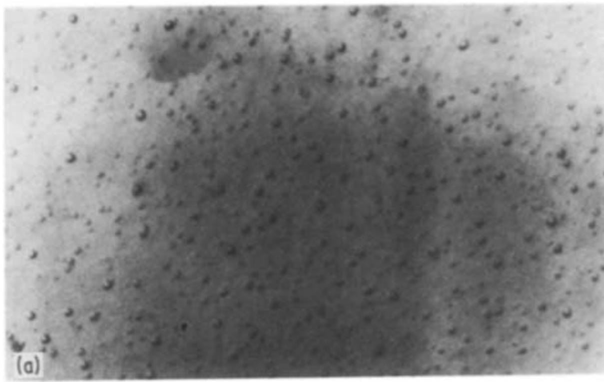
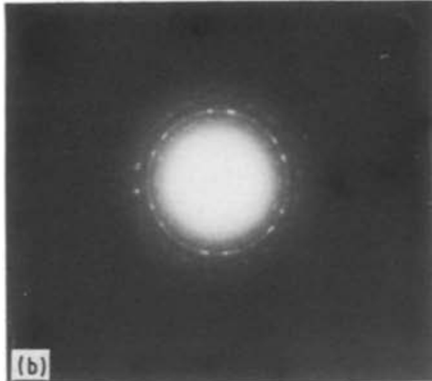
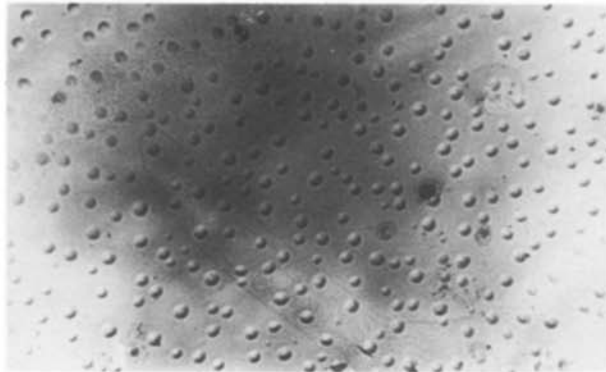
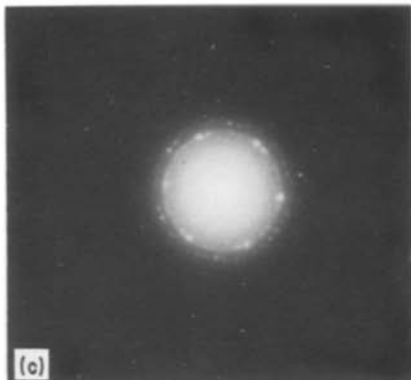
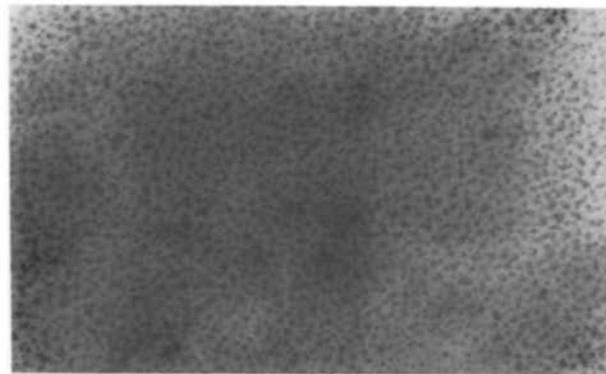


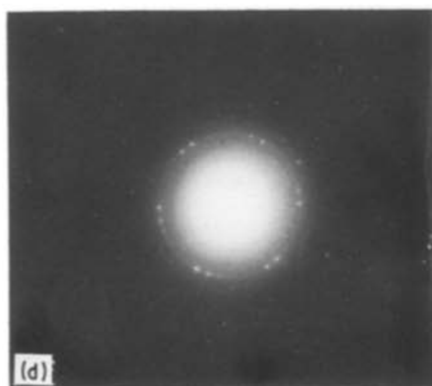
Figure 4 Transmission electron micrographs and transmission electron diffraction patterns of vanadium deposits on carbon substrate (a) 10 nm in thickness, × 7280 (b) 15 nm in thickness, × 5800 (c) 22 nm in thickness, × 7280 (d) 30 nm in thickness × 14000.

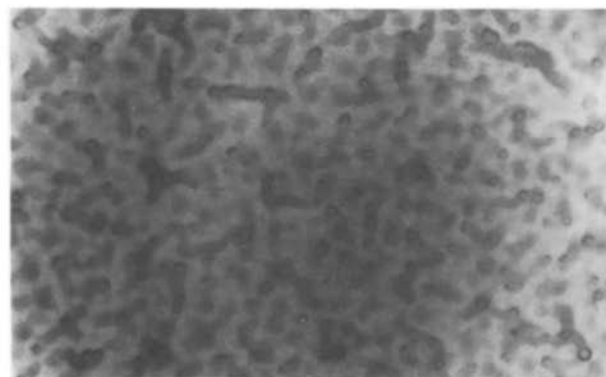












advantage. The details of nucleation and growth depend on the materials being deposited and on parameters such as substrate material and temperature, the rate of deposition, and the angle of incidence of the evaporant onto the substrate [19]. In general when a film is deposited on any substrate in vacuum by evaporation, the nucleation of the deposited film begins at any different nucleation sites, usually at imperfections in the substrate surface as a result of the loss of the high mobility of arriving particles at such sites. Additional particles arriving from the source agglomerate about the nuclei, and an island structured film is formed. As the deposition continues, islands coalesce decreasing the island density. The islands then grow until contact is made with neighbours, and gradually the voids between the agglomerates are filled producing a filament like network. Eventually, a macroscopically uniform thin film is obtained [20].

Vanadium films have been deposited on amorphous carbon substrate with an evaporation rate at 3 nm

sec^{-1}. The first visible picture appears, having an archipelago structure as shown in Fig. 4a The archipelago stage in which the film appears as a collection of widely separated islands. On this picture nuclei with sizes ranging from 12 to 15 nm diameter are observed. The lower limit is due to the lack of contrast of the smaller nuclei [20]. It was found that by increasing the film thickness to 15 nm a coalescence between a few nuclei occurred. This means that the nuclei attached to each other forming large grains with diameter 25 nm, while other workers [1] found it to be 20 nm. In this picture the differences in transmission of large and small nuclei are clearly visible (Fig. 4b). By further increasing the film thickness, the archipelago structure has changed into a labyrinth structure, in which a structure of connected islands is found with a labyrinth of canals separating them. In Fig. 4d the following details can be observed.

(a) The canals are of strikingly uniform width.

(b) In the canals small nuclei are found.

(c) The original round nuclei have been combined into larger agglomerates.

A sequence of electron diffraction patterns associated with the transmission electron micrographs of Fig. 4 shows that each deposit consists mainly of continuous rings composed of numerous spots. It is well known that substrates of amouphous structure have been considered as neutral substrates [21]. They have practically no effect on the formation, growth and orientation of the crystals condensed on them. Accordingly, it can be assumed that any orientation in layers deposited on these substrates is an indication of the influence of the other factors such as the direction of the stream of atoms or molecules during evaporation, relative velocity of growth of individual faces, recrystallization and contamination.

Rock salt crystals were used as a substrate for this work because the cleavage surface is smooth on an atomic scale. The dimensions of the desired area need only be in the order of a micron so that growth of a film over the area will not be influenced by edge effects. Also, it is possible to detach the deposits from the substrate by dissolving the substrate when preparing self-supported films. As rock salt is deliquescent hence the substrate must be mounted on holders and placed under vacuum as soon as possible after cleavage in air.

A sequence of the transmission electron micrographs, Fig. 5, shows the various stages of growth of vanadium films deposited onto the cleavage surface of a rock salt. The electron micrographs indicated that initially the films formed as large numbers of discrete particles. These particles then grow to form observable islands whose shapes are determined by interfacial energies and deposition conditions. The growth is diffusion-controlled, that is, adatoms and subcritical clusters diffuse over the substrate surface and are captured by the stable islands. Further increasing the thickness results in aggregates of opaque grains being observed. In this case, the resulting coalescence leads to the formation of very fine crystals with sharp

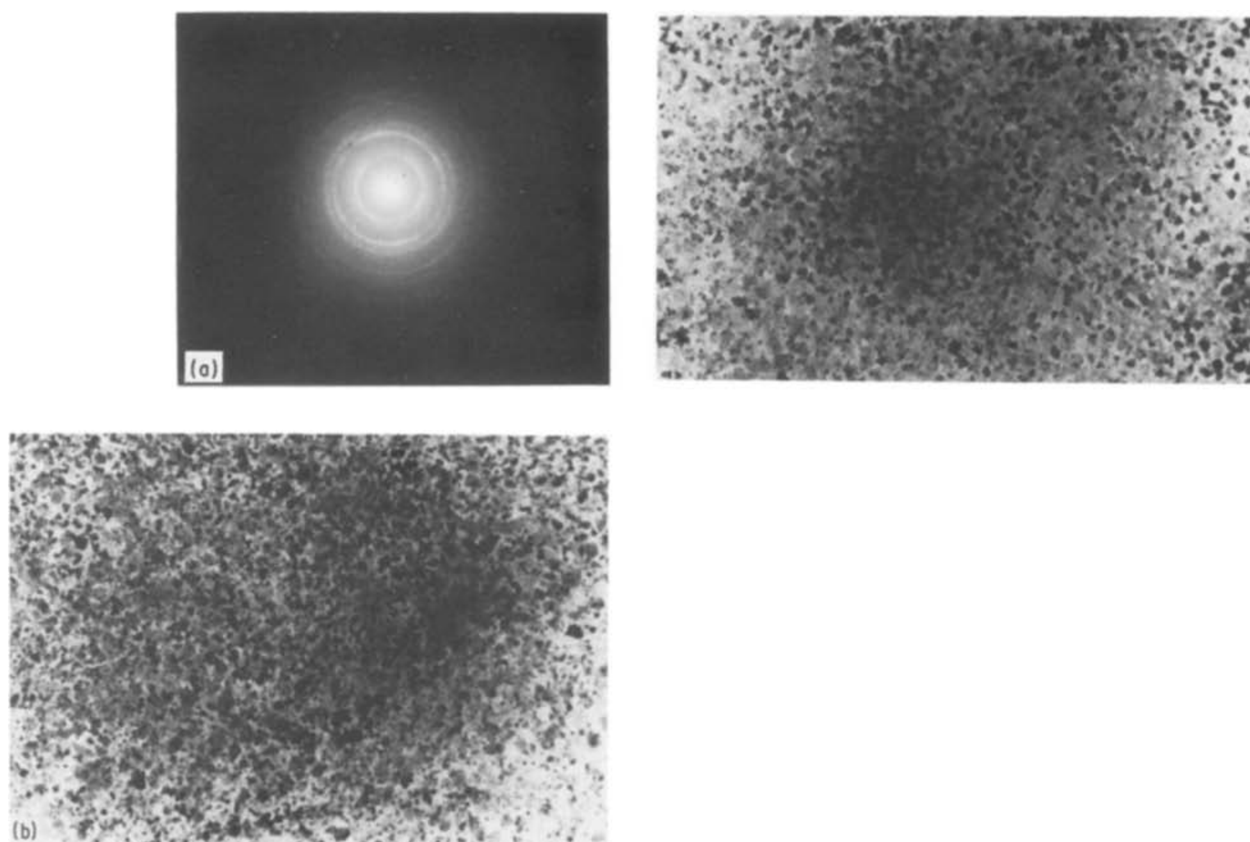
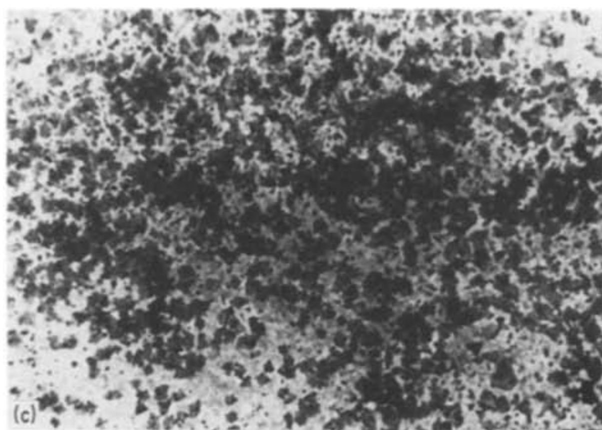
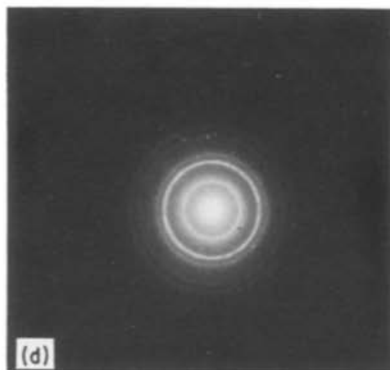
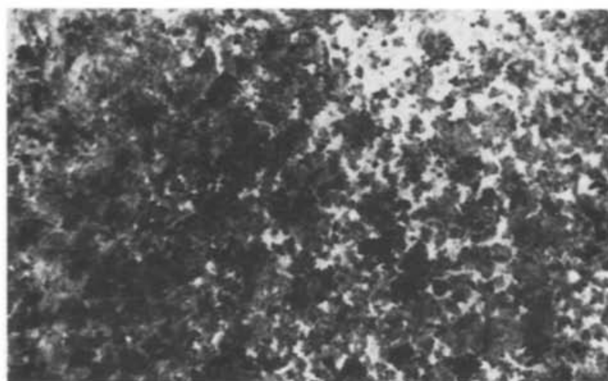
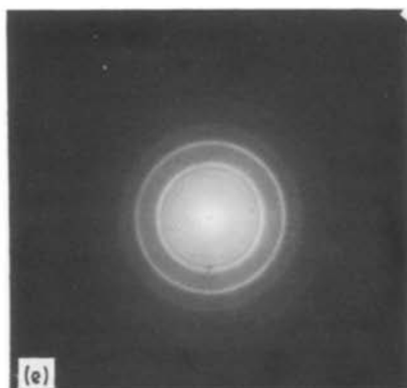


Figure 5 Transmission electron micrographs and transmission electron diffraction patterns of vanadium deposits on a cleaved surface of a rock salt crystal (a) 20 nm in thickness, × 9100 (b) 30 nm in thickness, × 9100 (c) 50 nm in thickness, × 9100 (d) 70 nm in thickness, × 9100 (e) 80 nm in thickness, × 9100.









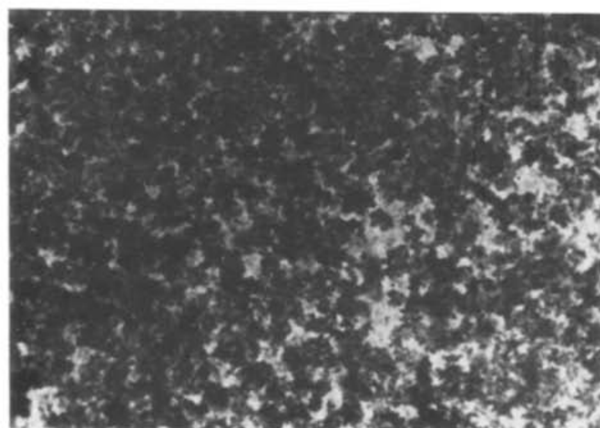


Figure 5 Continued.

geometrical shape and larger size as compared with forementioned stages (Fig. 5c). Finally a continuous thin film is formed. Aggregates of dark and transparent particles can be observed in this film. The variation in contrast between the transparent and dark areas arises solely from differences in orientation from grain to grain, the film is uniformly thick over the area shown. Since the diffracted beams are stopped off by the objective aperture, dark grains correspond to areas which are in a strong diffracting position [22]. Moreover, in this film small irregular holes are also observable.

A sequence of transmission electron diffraction patterns associated with the transmission electron micrographs of Fig. 5 shows that the deposited vanadium films have a polycrystalline structure and consist of aggregates of vanadium crystals randomly oriented on the rock salt substrate.

References

1. J. E. NESTELL, JR., R. W. CHRISTY, MITCHELL H. COHEN and G. C. RUBEN, *J. Appl. Phys.* **51** (1980) 655.
2. O. S. HEAVENS, "Optical Properties of Thin Solid Films" (Butterworths, London, 1955).
3. G. V. ROZENBERG, "Optics of Thin Films" (Fitzmatgiz, Moscow, 1958).
4. G. CHASSAING, P. GRAVIER, M. SIGRIST and R. PIERRISNARD, *Solid State Commun.* **15** (1974) 1613.
5. M. SIGRIST, G. CHASSAING and P. GRAVIER, *ibid.* **17** (1975) 647.
6. G. CHASSAING, P. GRAVIER and M. SINGRIST, *Thin Solid Films* **35** (1976) 125.
7. M. YASUI, E. HAYASHI and M. SHIMIZU, *J. Phys. Soc. Jpn.* **29** (1970) 1446.
8. D. L. MISELL and A. J. ATKINS, *Phil. Mag.* **1** (1973) 95.
9. L. FIERMANS and J. VENNIK, *Phys. Status Solidi* **41** (1970) 621.
10. V. F. ORMONT, "Structure of Inorganic Substances

GITTL", (Moscow, 1950).
11. V. G. PYN'KO, L. I. KVEGLIS and V. S. KORCHMAR, *Soviet Physics-Solid State* **13** (1972) 2800.
12. P. B. JOHNSON and R. W. CHRISTY, *Phys. Rev. B (USA)* **9** (1974) 5056.
13. Y. SAITO, S. YATSUYA, K. MIHAMA and R. UYEDA, *J. Cryst. Growth* **45** (1978) 501.
14. K. KIMOTO, *J. Cryst. Soc. Jpn.* **14** (1972) 119.
15. S. TOLANSKY, in "Introduction to Interferometry" (Longmans Green & Co. London, New York, Toronto, 1955) 157.
16. L. G. SCHULZ, *J. Opt. Soc. Amer.* **43** (1953) 406.
17. M. R. TUBBS, *Proc. R. Soc. London* **A288** (1964) 566.
18. W. H. BRATTAIN and H. B. BRIGGS, *Phys. Rev.* **75** (1949) 1705.
19. Z. H. MEIKSIN, *Phys. of Thin Films* **8** (1975) 99.
20. J. VAN DE WATERBEEND, *Philips. Res. Repts* **21** (1966) 27.
21. Z. G. PINSKER, "Electron diffraction", (Butterworths, London, 1953).
22. G. THOMAS, "Transmission electron microscopy of metals", (John Wiley & Sons., Inc., New York, 1962).

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