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Growth and morphology of cadmium oxide whiskers

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A way of growing cadmium oxide whiskers is described. The whiskers were grown on CdS single crystal substrates having a palladium film ($d \sim 10$ to 30 nm) deposited on the surface, upon annealing of the samples in an argon atmosphere with small oxygen impurity, at temperatures 580 to 640° C, for 2 to 4 h. The whiskers have micron sizes: a cross-section of several square micrometres, length from several tens to several hundreds of micrometres. The composition (CdO) and structure of the whiskers have been determined by X-ray microanalysis and reflection high energy electron diffraction. The main crystal forms studied by SEM, are described: tetragonal prisms, needles, threads, prisms with a faceted formation on the upper base, plates. On the basis of the data from electron diffraction and SEM as well as the comparison with literature data, it is established that the predominant orientation of growth is ⟨1 0 0⟩.

1. Introduction

Among the group of cadmium chalcogenides, cadmium oxide is comparatively the least studied. Data for thorough and systematic studies on the properties of cadmium oxide crystals are not found in the literature. This is explained by some authors [1–3] as not so much the result of insufficient interest in them but as a result of the difficulties in obtaining them.

Various methods have been used to grow cadmium oxide single crystals, for instance from vapour phase [1, 2, 4–8], from the melt [1], through sublimation [9, 10], or floating zone technique [1]. The single crystals obtained by these methods have a maximum size of 10 to 12 mm and only one paper [2] points to a size of 20 mm.

The pursuit of obtaining single crystals of larger size suitable for electrical, optical and other measurements has shifted the interest from small crystals, whiskers, and maybe that is why only a few papers supply information on cadmium oxide whiskers. Fischer and Spear [11] only state that they have obtained small dark-red whiskers under definite conditions in their experiments for growing cadmium oxide single crystals. Houten [12] has obtained cadmium oxide needles through decomposition of cadmium oxalate on heating it in air and oxidation of the cadmium obtained. Kumar [3] has obtained dendrites and needle-like crystals by molten hydrous KOH solutions. A more detailed description of small crystals shaped as needles, plates, cubes, swords and twinned dendrites is given by Hayashi [13]. No information, however, has been found in the literature concerning the study of the composition and morphology of cadmium oxide whiskers.

The present paper discusses a way of obtaining

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cadmium oxide whiskers previously not described in the literature as well as the results of studies on the morphology and composition of the whiskers carried out by scanning electron microscopy (SEM), reflection high energy electron diffraction (RHEED) and X-ray microanalysis.

2. Experimental details

Cadmium oxide whiskers have been obtained in the following way: a thin palladium film has been deposited on the surface of single crystal substrates of cadmium sulphide and the obtained specimens have been annealed in an argon atmosphere. Under these conditions whiskers have grown on the substrates.

Thin single crystal plates of cadmium sulphide have been used as substrates. They were obtained on the walls of a quartz tube from the gas phase through sublimation of powdered cadmium sulphide ("Merk"–Darmstadt) in an argon stream. Single crystal plates of cadmium sulphide with a thickness of 20 to 100 μm, face of $\{11\bar{2}0\}$ type, hexagonal structure and good stoichiometry have been used. The crystal surface has not been specially treated prior to the deposition of palladium. The film of palladium with 10 to 30 nm thickness, measured by a X-ray spectral method [14], has been deposited by vacuum evaporation.

The annealing of the cadmium sulphide–palladium system has been performed in a quartz tube at a slow stream of technically pure argon. The annealing temperature for various groups of specimens has been varied from 580 to 640° C. The duration of annealing for the separate groups of specimens has been varied from 2 to 4 h. These conditions have been established as optimal for whisker growth.

In order to clarify the role of the palladium film, comparative experiments have been carried out with substrates of which only part of the surface has been covered with palladium and other substrates not covered with palladium at all.

The morphology and composition of the whiskers have been studied with the aid of a scanning electron microscope JEOL, JSM 35 at an accelerating voltage of 15 kV, through RHEED by Hitachi HU 11 A electron microscope at an accelerating voltage of 75 kV and by a two-channel X-ray microanalyser JEOL 35 DDS with analysing crystals, STE (stearat, $Pb(C_{18}H_{35}O_2)_2$ for oxygen and PET (pentaeretrit, $C_5H_{12}O_4$) for cadmium.

Qualitative and quantitative X-ray microanalyses have been carried out on whiskers with a width about 10 μm and thickness about 2 μm as well as on the surface of cadmium sulphide substrates (covered or not covered with palladium, annealed or unannealed). The conditions of the analysis have been accelerating voltage of 15 kV and absorbed electron current 1×10^{-7} A. As standards CdS, SiO_2 and SiO crystals as well as pure cadmium have been used.

The correction for the atom number Z has been calculated after Poole and Thomas [15] and for the absorption A according to Philibert [16] with mass absorption coefficients for oxygen after Henke [17] as well as for the remaining elements, after Heinrich [18].

Under these conditions the calculated value of the depth in the crystal X from which the Cd$L\alpha$ radiation is registered is $X \cong 1\,\mu$m (at density $\rho_{CdO} = 8.2\,g\,cm^{-3}$) and for the O$K\alpha$ radiation it is $X \cong 0.2\,\mu$m. In view of this, the measured whiskers having a thickness of about 2 μm represent infinitely thick films or bulk samples at the conditions at which the quantitative analysis is performed.

3. Results

The whiskers obtained under optimal conditions and observed with the aid of an optical microscope (magnification 50 to 100 times) look like an interlace situated on a granular surface. The density of the whiskers in various regions of the crystal substrate is different, which makes it difficult to estimate their average number on a unit area. The base together with the whiskers is easily separated from the crystal substrate. The whiskers have yellow-orange to brown colouration, in some cases they are grey-black. After separation of the whiskers and their base, the surface of the substrate looks strongly damaged, rough and bright-yellow in colour. The change in the colour of cadmium oxide crystals from black or grey [1, 3, 11, 19], red or dark brown [19, 20] to yellow [19] is explained by the authors with a varying quantity of excess cadmium in interstitial positions [2, 11, 13, 20, 21].

3.1. Composition and structure of the whiskers

The qualitative analysis of the whiskers and of the granular base on which they grow indicate the presence only of cadmium and oxygen. Palladium

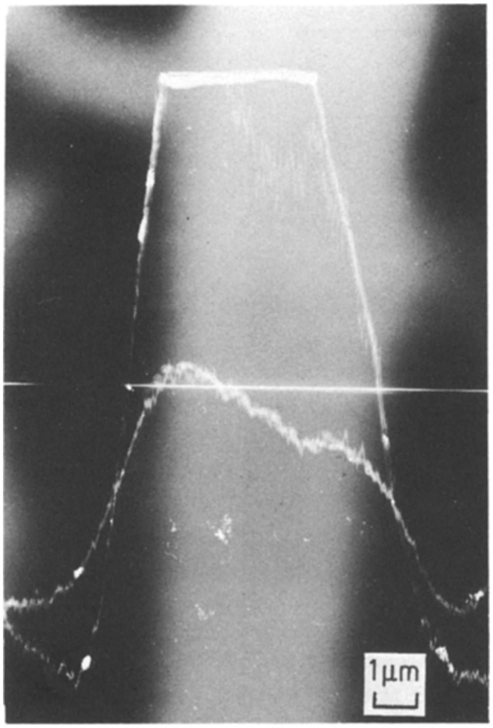


Figure 1 SEM-microphotograph of a whisker in back-scattered electrons and concentration profiles of distribution of cadmium and oxygen.

has not been registered with the sensitivity range of the equipment. Fig. 1 shows a SEM photograph of a whisker in back-scattered electrons as well as the concentration profiles of cadmium and oxygen distribution.

The results from the quantitative analysis of the whiskers are given in Table I, where K_O are the empirically obtained ratios of the intensities of $OK\alpha$ from a whisker and from the standard samples, SiO_2 and SiO; K_{Cd} are correspondingly the ratios for $CdL\alpha$ at CdS and cadmium standards; C_O and C_{Cd} are the weight concentration values of oxygen and cadmium. In the last column the relative deviation from the stoichiometric composition of CdO is given. These results are an evidence that these are CdO whiskers.

The inference concerning the composition of the whiskers based on the results from X-ray microanalysis has been confirmed by the electron diffraction analysis as well. Fig. 2 shows RHEED patterns of the surface of a specimen with whiskers. The data for the interplanar distances obtained from the Debye rings (Fig. 2a) coincide very well with the data for cadmium oxide with a lattice of NaCl-type ($a = 0.46953$ nm) for planes 111, 200, 220, 311, 222, 331, 400, 420 and 422. No reflexes have been found corresponding to palladium and its compounds with sulphur as well as those corresponding to cadmium sulphide. An idea for the orientation of part of the whiskers could be gained from the electron-diffraction pattern in Fig. 2b. It shows an orientation of the whiskers along ⟨100⟩ perpendicular to the substrate.

3.2. Morphology

A general view of the surface of a cadmium sulphide substrate with whiskers is seen on the stereopair in Fig. 3.

The typical crystal forms of the whiskers established from the micrographs can be generalized as follows:

1. Tetragonal prisms (with quadratic or rectangular cross-section) (Fig. 4). In some cases the upper base of the prism is faceted with faces different from the prismatic ones (Fig. 4b). The mean length of this type of whiskers is 10 to 20 µm, the other two sizes being of the order of 1 to 3 µm.
2. Needles (Fig. 5) faceted and unfaceted, with thickness varying along the length and ending with a sharp point shaped as a cone or a pyramid. The length of this type of whisker may reach 20–50–100 µm, the size of the base being slightly smaller than that of prismatic crystals.
3. Threads (see for example Fig. 6d) have an

TABLE I Values of the ratios of the intensities, the weight concentration and the relative deviation from the stiochiometric composition

Standard	K_O	K_{Cd}	C_O	C_{Cd}	Relative deviation from the stoichiometric composition of CdO (%)
SiO_2	0.103	–	0.123	–	0.4
SiO	0.179	–	0.124	–	0.4
CdS	–	1.120	–	0.865	1.1
Cd	–	0.845	–	0.880	0.5

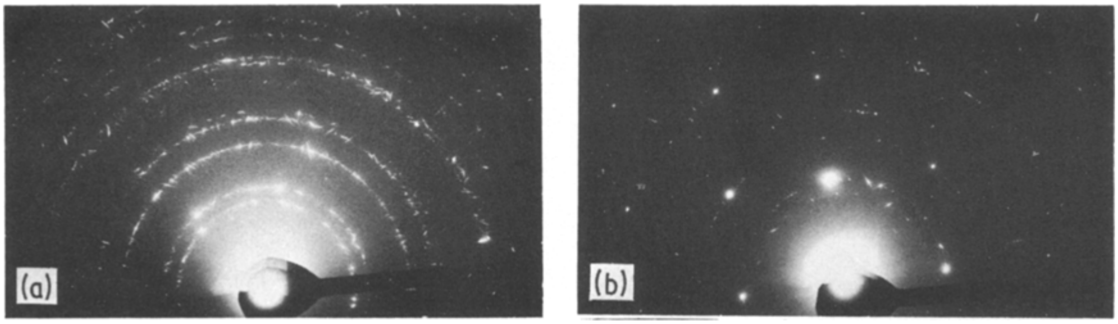


Figure 2 Electron diffraction patterns of the surface of a cadmium sulphide–palladium specimen covered with whiskers, (a) electron diffraction pattern with Debye rings and (b) electron diffraction pattern with spot reflexes.

even greater length to thickness ratio but their cross-section is unchanged along the thread length.

4. Prisms ending with a well faceted formation on the upper base occur in three varieties: (a) whiskers with a size close to that of the needles whose length of the prismatic part is much greater than that of the faceted formation on the upper base (Fig. 6a); (b) whiskers whose prismatic part and faceted formation have an approximately equal length, the prismatic part being replaced by a pyramidal one (Fig. 6b); and (c) whiskers of type (b) but with a constant cross-section of the prismatic part (Fig. 6c). In some cases the faceted formation on the upper base shows a tendency towards a complicated faceting (Fig. 6d).

5. Plates. A typical example of a plate is shown in Fig. 7.

Other morphological peculiarities of the whiskers and the surface of the single crystal substrates are the ramifications and the faceted grains. Figs. 8a, b and c present several varieties of such ramifications. Fig. 8b demonstrates an interesting peculiarity of the faces of prismatic whiskers which are smooth at small magnifications. Larger magnifications show that the faces are covered with roughnesses of 50 to 100 nm in size. Sometimes on the surface of the whiskers striations are observed.

The base on which the whiskers grow usually resembles a granular mass with faceted grains (see for instance Figs. 3 and 4a). X-ray microanalysis has proved that these grains are also of cadmium oxide. In some cases the base consists of tiny whiskers (thickness 10 to 20 nm) with a high density (Fig. 9).

3.3. Effect of palladium film, temperature and ambient gas on the growth of whiskers

The morphology of the whiskers and of the base from which they grow, described in the preceeding Section, refers only to the case of cadmium

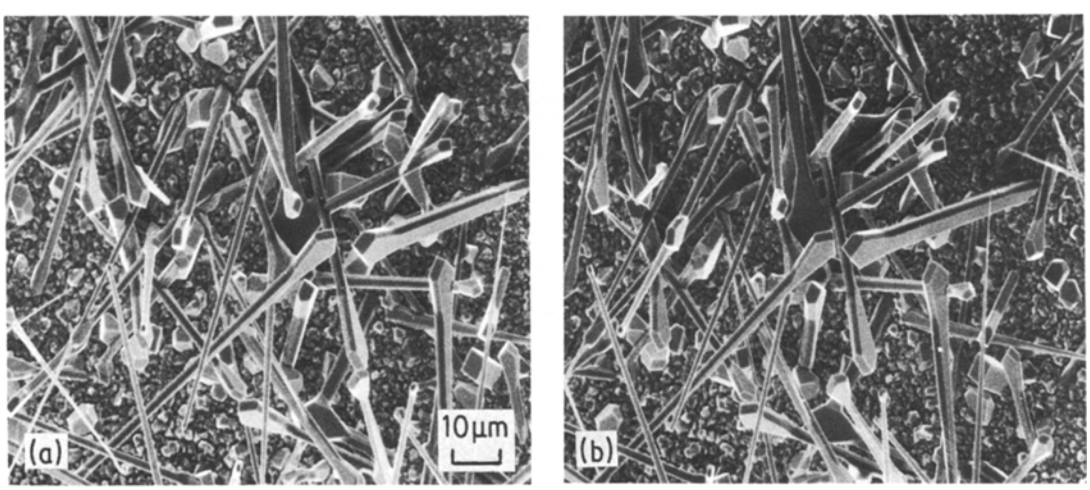


Figure 3 SEM-stereopair micrographs of cadmium oxide whiskers grown on a cadmium sulphide substrate ($\theta = 5°$).

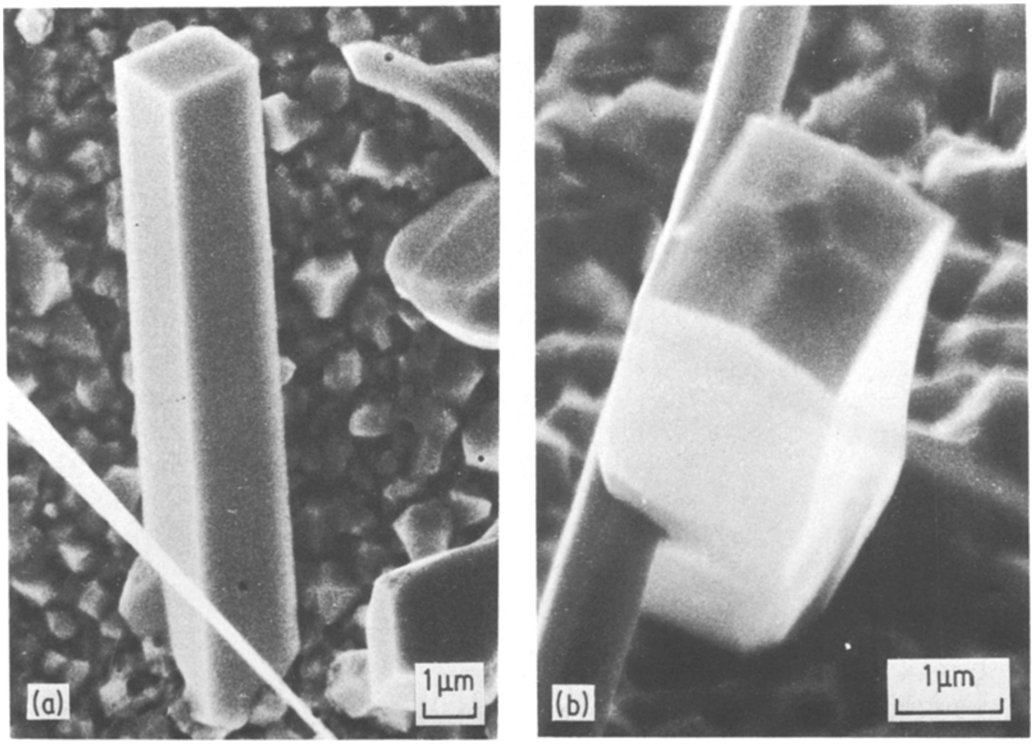


Figure 4 Whiskers in the form of a tetragonal prism (a) with unfaceted and (b) with faceted upper base.

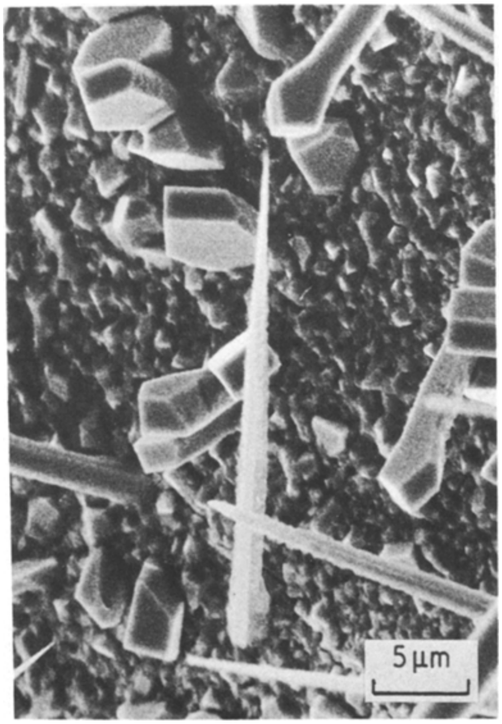


Figure 5 Whisker in the form of a needle.

sulphide substrate covered with palladium. The experiments made with cadmium sulphide substrate partially covered with palladium show that cadmium oxide whiskers grow only on the surface covered with palladium. Fig. 10 presents a micrograph of the boundary between the surfaces covered and not covered with palladium (at two different magnifications). On the surface of the cadmium sulphide substrate not covered with palladium, separate unfaceted grains are grown which the X-ray microanalysis has identified as cadmium oxide ones as well.

Whiskers do not grow at relatively low temperatures, below 480° C, even if annealed for up to 20 h, with the remaining conditions within the range of the optimal ones. On the other hand very few whiskers grow at relatively high temperatures, around 690° C.

On changing the composition of the ambient gas it has been established that whiskers with low density grow in air while in vacuum 10^{-5} torr, no cadmium oxide whiskers grow upon heating for up to 16 h. In an atmosphere of flowing hydrogen no whiskers grow; with these conditions the single

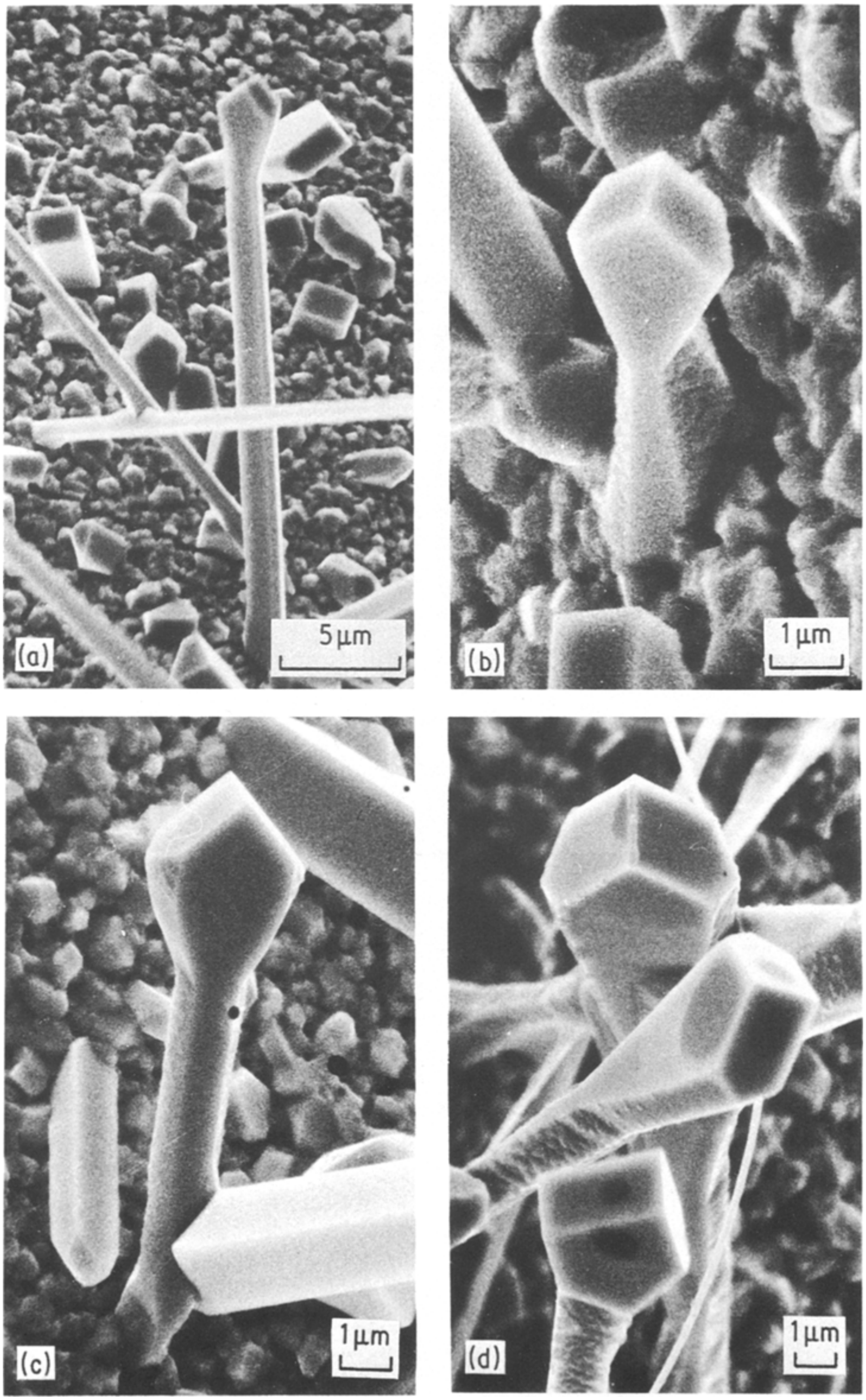


Figure 6 Whiskers in the form of prisms ending with a faceted formation, in three varieties (a) to (c) and complicated faceting (d).

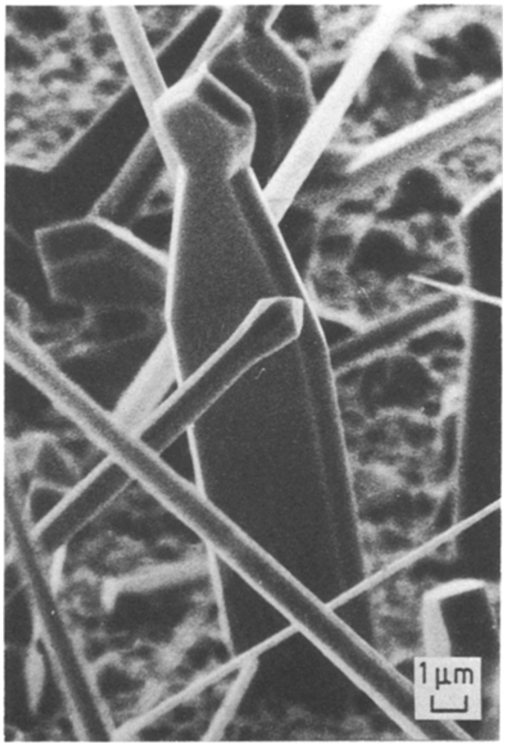


Figure 7 Whisker in the form of a plate.

crystal substrates are dissociated, destructed and, upon heating for more than 1 to 2 h, they completely disappear from the quartz tube.

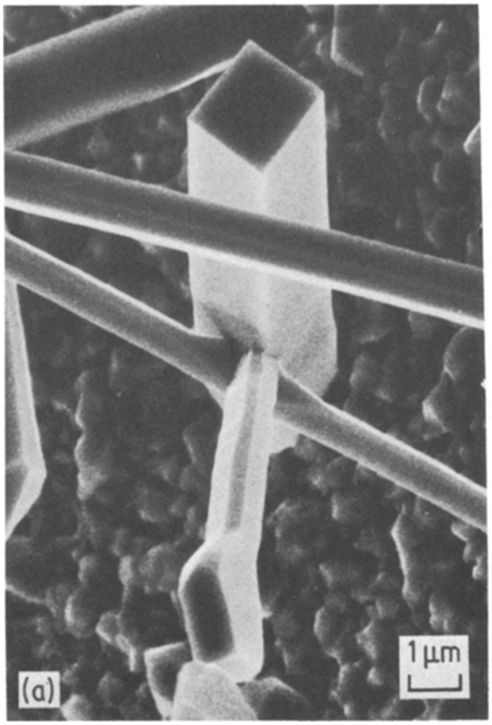
4. Discussion

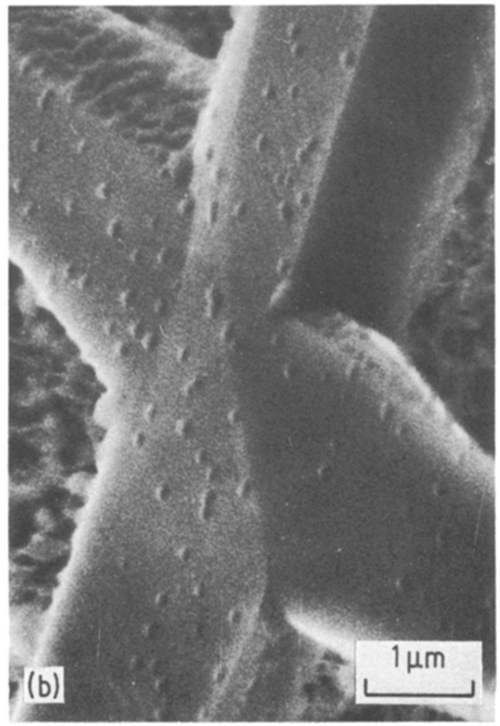
The method for obtaining cadmium oxide whiskers, described in Section 2, is in experimental terms very close to one of the methods for the doping of semiconductor single crystals with metals, namely by thermal diffusion, as well as to the Gilles and van Cakenberghe [22] method for recrystallization of films. The deposition of thin metal films on a single crystal substrate is employed also in the practice of growing whiskers according to the VLS-mechanism [23]. Obviously, the palladium film together with the other factors, namely orientation of the single crystal substrate, ambient gas, temperature and duration of annealing, is one of the main factors determining the growth of whiskers. This inference is supported by the comparison of the results from the experiments concerning the surface of cadmium sulphide substrates covered and non-covered with palladium.

A number of authors have observed cadmium oxide on the surface of cadmium sulphide films and single crystals. Cadmium oxide has been established on the surface of cadmium sulphide films in the course of obtaining the films through evaporation in vacuo [24]. After heating cadmium sulphide films and single crystals in an oxygen atmosphere, air and nitrogen or argon in the temperature range of 400 to 600° C, cadmium oxide has been found on their surface [25–28]. The experimental conditions nearest to those used in the present investigation are the conditions of Shalimova *et al.* [26]. They have found that at recrystallization of cadmium sulphide films after the Gilles and van Cakenberghe [22] method, with a thin silver film in argon, nitrogen and air, a cadmium oxide is obtained even at temperatures of 450 to 480° C being formed in large quantity at 500 to 600° C.

The formation of cadmium oxide can be considered as a result of cadmium sulphide oxidation. This process has been discussed in detail by Chizhikov [29]. The process of oxidation has been presented by this author as a series of reactions proceeding simultaneously and consecutively with cadmium sulphate and free cadmium as intermediate products. Depending on the temperature and the percentage of oxygen in the ambient gas (in this case nitrogen) one or other chemical reaction is favoured leading to various ratios between the intermediates and the end product. Up to 300° C, a cadmium sulphate is predominantly formed while upon increasing the temperature up to 700° C, the obtaining of structurally free cadmium oxide is increased even at insignificant oxygen content (0.5%). In the case discussed, the temperature interval in which cadmium oxide whiskers are obtained falls within the range of temperatures considered by Chizhikov. The argon used in the present experiments contains a small, uncontrolled quantity of oxygen (not less than 0.1%). The duration of heating also corresponds to Chizhikov's data. In view of this we may assume that a mechanism and kinetics of cadmium sulphide oxidation analogous to those described by Chizhikov [29] are also valid here.

The role of the palladium film in the growth of cadmium oxide whiskers probably consists, on one hand, in creating favourable conditions for VLS-mechanism of growth [23] through formation of an eutectic drop of cadmium–palladium at the top of the whisker (m.p. 320.32° C for 0.3 at% of palladium) and on the other, in accelerating the oxidation process owing to the catalytic action of palladium.





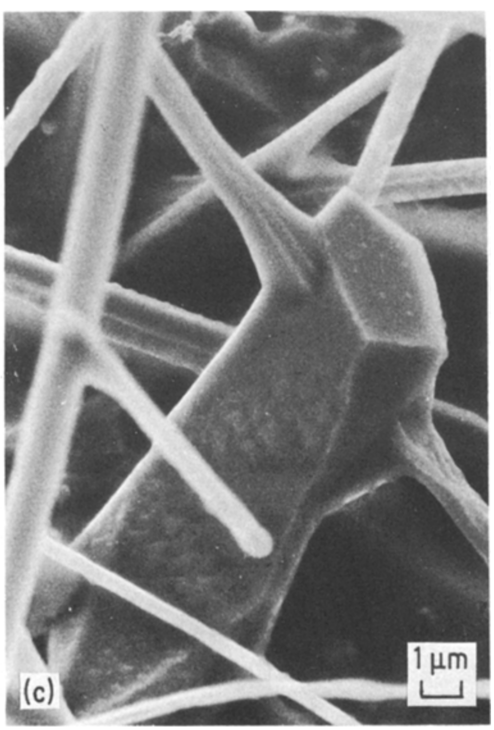


Figure 8 Complicated forms of whiskers-ramifications (a) to (c).

The above-mentioned experimental fact that on heating in vacuo, cadmium oxide whiskers do not grow, could be explained by an insufficient oxygen quantity for the realization of the indicated mechanism and kinetics of oxidation. The destruction and disappearance of the crystals on heating in hydrogen is obviously due to the restoring reaction to cadmium sulphide [29].

The orientation of the substrate proved essential for the growth of whiskers. This growth is insignificantly for unoriented plates cut out of a bulk single crystal and absent for sintered cadmium sulphide tablets. Probably, on the prismatic faces $\{11\bar{2}0\}$ of the single crystal substrates more favourable conditions are created for the appearance of oriented nuclei from which whiskers are growing.

The data for a cubic structure of the whiskers obtained by RHEED analysis are in good agreement with those in the literature. It is known that cadmium oxide has a cubic lattice of the NaCl-type (with a lattice parameter $a = 0.46953$ nm [30], and it has been determined and referred to as such by a number of authors [1–3, 11–13, 20, 21, 29, 31]. Only one paper [25] reports the obtaining of hexagonal cadmium oxide (with lattice parameters $a \doteq 0.326 \pm 0.05$ nm and $c = 0.522 \pm 0.007$ nm) produced after heating of epitaxial cadmium sulphide films under an enriched mixture.

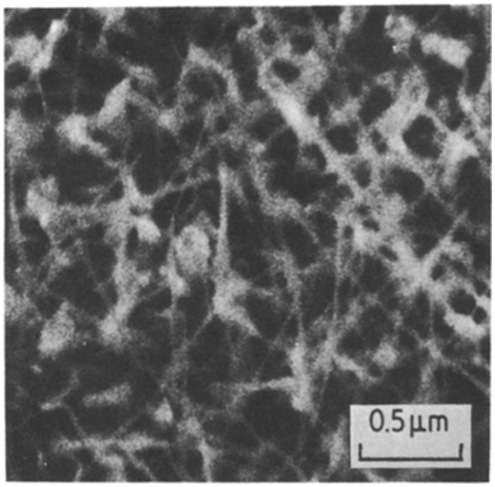


Figure 9 Base with whiskers of small sizes and high density.

The equilibrium planes for the simple cubic lattice theoretically established by Honigmann [32] as well as Wolff and Gualtieri [33] are {100}, {110}, {111} and {211}.

Ivanov and Savitskaya [5] and Ivanov *et al.* [6, 34] in studying the morphology of cadmium oxide single crystals obtained from a vapour–gas phase, have determined some basic crystal forms, such as: cube, skeleton-cube, cuboctahedron, octahedron, prism, prismatic hexagonal needle, pyramidal needles, needle with a plate. Orientation ⟨111⟩ has been found as preferential in growth of crystals. Only the growth of the plates along ⟨100⟩ is an exception. The crystals forms observed are faceted by habitus planes of {100}, {111}, and {110} types. In the crystal forms observed by Hayashi [13] namely needles along ⟨111⟩, plates, swords, dendrites along ⟨110⟩ and ⟨100⟩ the faces through which these forms are demonstrated involve {100}, {111} and {211}. Fischer and Spear [11] have found that the crystals they have obtained are faceted by {100} and {111} faces. The needles of Van Houten [12] grow also along ⟨111⟩. Kořàk and Höschl [10] and Kumar [3] report also {100} and {110} as habitus planes of the crystals grown by them. The forms observed by Kumar [3] are octahedrons, hopper-like crystals and dendrites along ⟨100⟩. The nuclei studied by Sergejeva *et al.* [28] are octahedrons with [001] texture

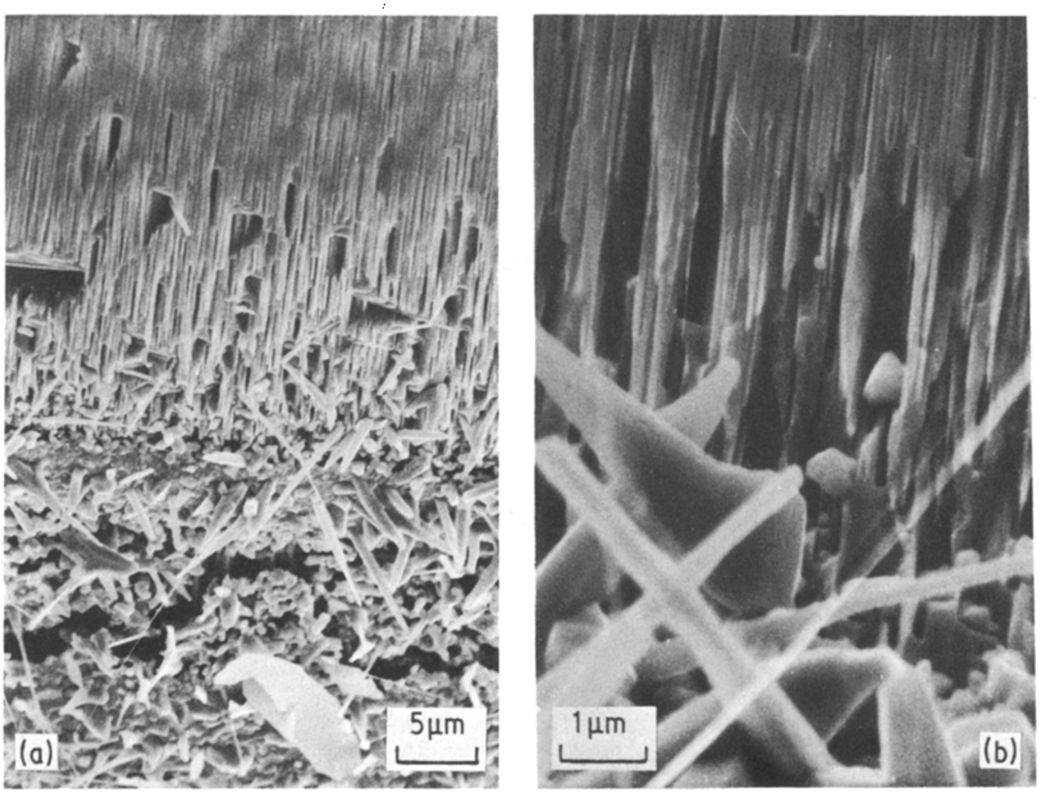


Figure 10 Single crystal substrate of cadmium sulphide partially covered with palladium, after heating; boundary between covered and uncovered parts.

and flat triangles with (111) plane parallel to the substrate. To the observed habitus faces can be added to figures obtained by etching cadmium oxide crystals [35] faceted by {110} and {111} planes. The available literature data show that with cadmium oxide crystals, experimentally are observed all equilibrium planes predicted by the theory.

The prismatic whiskers discussed in the present paper (Fig. 4) unlike the prismatic hexagonal needles grown along ⟨111⟩ and described by Ivanov *et al.* [6], are tetragonal. Most probably, these whiskers grow along ⟨100⟩ being walled by {100} faces as reported by Givargizov [23] for whiskers with a lattice of NaCl-type. This same inference refers also to the prisms ending with a faceted formation (Fig. 6). The faceted upper base of the prismatic whiskers is presumably faceted with faces of {110} type [36]. The plates (Fig. 7) are similar to those described by Ivanov *et al.* [6] faceted by planes of {100} type. The needles are not faceted by equilibrium planes and their faces appear rough owing to numerous steps which diminish their cross-section.

The roughness (Fig. 8b) on the faces of the whiskers are probably related to a stage of their growth during which not only their length but also their thickness is increased.

Other morphological peculiarities have also been established in the course of these observations which, together with the questions of the growth mechanism, the structure, the effect of various factors, need further studies and interpretations.

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