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Cadmium oxide whisker crystals grown by the vapour–liquid–solid mechanism using various elements as growth initiators

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CdO whisker crystals with micrometre thickness and length of up to 4.5 mm were grown by a simple technology described in previous publications of the authors. The whiskers grow on CdS crystal substrates, previously covered by a thin metal or silicon layer, on annealing in air at atmospheric pressure. The growth initiator used was Ag, Au, Al, Si, Mn, Ni, Pd or Pt. A study was carried out of the effect of impurities on the conditions and efficiency of growth, as well as on the morphology and composition of the whiskers obtained. The small crystals were examined using an optical microscope, a scanning electron microscope, X-ray structural analysis and X-ray microanalysis. The maximum speed of growth obtained with Au was about 1 mm h^{-1}. The whiskers grow with a face-centred cubic lattice. The largest crystals are in the form of a parallelipiped with facets of $\{1\,0\,0\}$. Data are obtained which support the vapour–liquid–solid mechanism of crystal growth. The possibility is also shown of growing whiskers on zinc or cadmium plates covered with a thin layer of Cu, Ag, Au or Al by applying the same technology.

1. Introduction

Data on the growth and properties of thread-like crystals (whiskers) of CdO are very scarce [1, 2]. A method has been proposed [3] for growing CdO whiskers of micrometre thickness by annealing CdS crystals, previously covered with gold, in air at atmospheric pressure. The method is distinguished by the simplicity of the apparatus used and the high efficiency of crystal growth. Data supporting the vapour–liquid–solid (VLS) mechanism [4, 5] were obtained. It was established [3, 6] that the whiskers obtained are too highly resistive, unlike the bulk CdO crystals which have an almost metallic conductivity [7]. The small conductivity of the whisker crystals was accounted for by their high perfection and purity.

The present paper is an attempt to enlarge the possibilities of the method proposed earlier by substituting the gold used as a liquid-forming agent by various other metals – silver, aluminium, manganese, nickel, palladium, platinum, or silicon.

The possibility was also tested of growing whiskers on a zinc or cadmium solid metal layer previously plated with copper, silver, gold, or aluminium.

2. Experimental procedure

The thread-like crystals were grown under the following conditions. The surfaces of CdS crystals, obtained from the gas phase with a size of approximately 5 mm × 2 mm × 0.1 mm, were layered with a thin (20–60 nm) metal or silicon layer by vacuum evaporation; they were then annealed in air at atmospheric pressure and at a steady temperature in the range 670–730 °C for 2–7 h; under these conditions, CdO whiskers grew on the CdS crystals. Almost the same procedure was carried out when samples of massive zinc or cadmium were used as substrates. The experimental set-up is presented in Fig. 1.

The composition and structure of the whiskers obtained were determined by X-ray structural analysis. The measurements were done on a DRON-2 diffractometer. Analyses were also performed on the substrates and on separate sectors of the whiskers by an

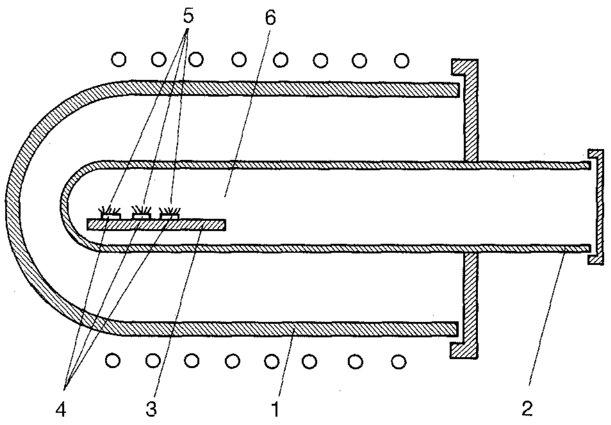

Figure 1 Experimental set-up: (1) oven, (2) quartz tube, (3) quartz plate, (4) CdS crystal substrates, (5) CdO whiskers, (6) air (pressure 1 atm).

SEM (Philips 515) with a Wedeax-3A X-ray microanalyser.

The whisker morphology was studied with an optical microscope and with the SEM.

3. Results

3.1. Conditions and efficiency of whisker growth

No whiskers grew when annealing was done of a CdS crystal whose surface had not been first layered with another substance [3]. In this case, only isomorphic CdO crystals grew (Fig. 2).

Whiskers grew in all cases when the surface of the CdS crystals was covered with a thin layer of one of the above-mentioned elements and the annealing in air was done under appropriate conditions of temperature and time (Table I). For the purposes of comparison, Table I includes also the results for Cu obtained by the authors in previous studies. The efficiency of growth determined by the whisker density (number of whiskers per unit area of substrate surface) and their size varies for the different impurities. It is greatest for Au and smallest for Cu, Si and Mn. These estimates were made by observations with an optical microscope with small magnification (62 ×). They are of an approximate character, since the density of the whiskers varies considerably in the different parts of one substrate, as well as in different substrates layered with the same metal.

The optimal temperature for whisker growth varies weakly in the cases of different impurities used as growth initiators and remains within the range 670–730 °C. The optimum duration of the process is 3–6 h.

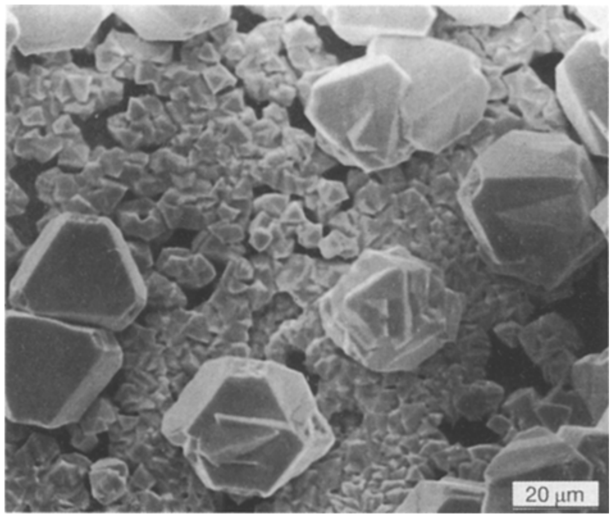

Figure 2 SEM micrograph of the surface of CdS crystal annealed in air without metal or any other coating: no whiskers but only isomorphic CdO crystals grow.

TABLE I Growth of CdO whiskers on CdS crystal substrate coated with a thin layer of impurity element

Substrate and coating	Group no. of impurity element in the periodic system	Whiskers obtained	Efficiency of growth
CdS without coating	–	No	–
CdS, Cu	I	Practically not	Poor
CdS, Ag	I	Yes	Good
CdS, Au	I	Yes	Very good
CdS, Al	III	Yes	Medium
CdS, Si	IV	Yes[a]	Poor
CdS, Mn	VII	Yes[a]	Poor
CdS, Ni	VIII	Yes	Medium
CdS, Pd	VIII	Yes	Good
CdS, Pt	VIII	Yes	Medium

[a] The composition of whiskers was not studied.

3.2. Composition and structure of whiskers

The composition of the thread-like crystals in the case of a CdS substrate and Ag, Au, Al, Ni, Pd and Pt used as impurities was CdO, established by X-ray structural analysis within the error limits (1–5%) of the method. CdO whiskers grow with a face-centred cubic lattice with a constant $a_0 = 0.4695$ nm. The largest crystals with size of approximately 2 mm × 0.1 mm × 0.01 mm, obtained with Au as an impurity, have the form of a parallelipiped with {1 0 0} faces.

The X-ray microanalysis showed that Al as an impurity was often established in whiskers, in concentrations from tenths of a per cent to 5–10%. On the other hand, Ag and Au as impurities are either not found or are present in much smaller concentrations of 0.1–1%. These two impurities were established either along the stem of the whiskers or in the spheres or sphere-like formations observed in a number of cases at the apexes of whiskers (see below).

3.3. Morphology

The typical crystal forms of the whiskers, as well as their size, depend significantly on the element used as growth initiator (Figs 3–9). There is a certain similarity in the forms and dimensions of whiskers obtained with metals of the same group of the periodic system, e.g. whiskers obtained with Ag as an impurity (Fig. 3) and with Au (Fig. 4), Ni (Fig. 7) and Pd (Fig. 8).

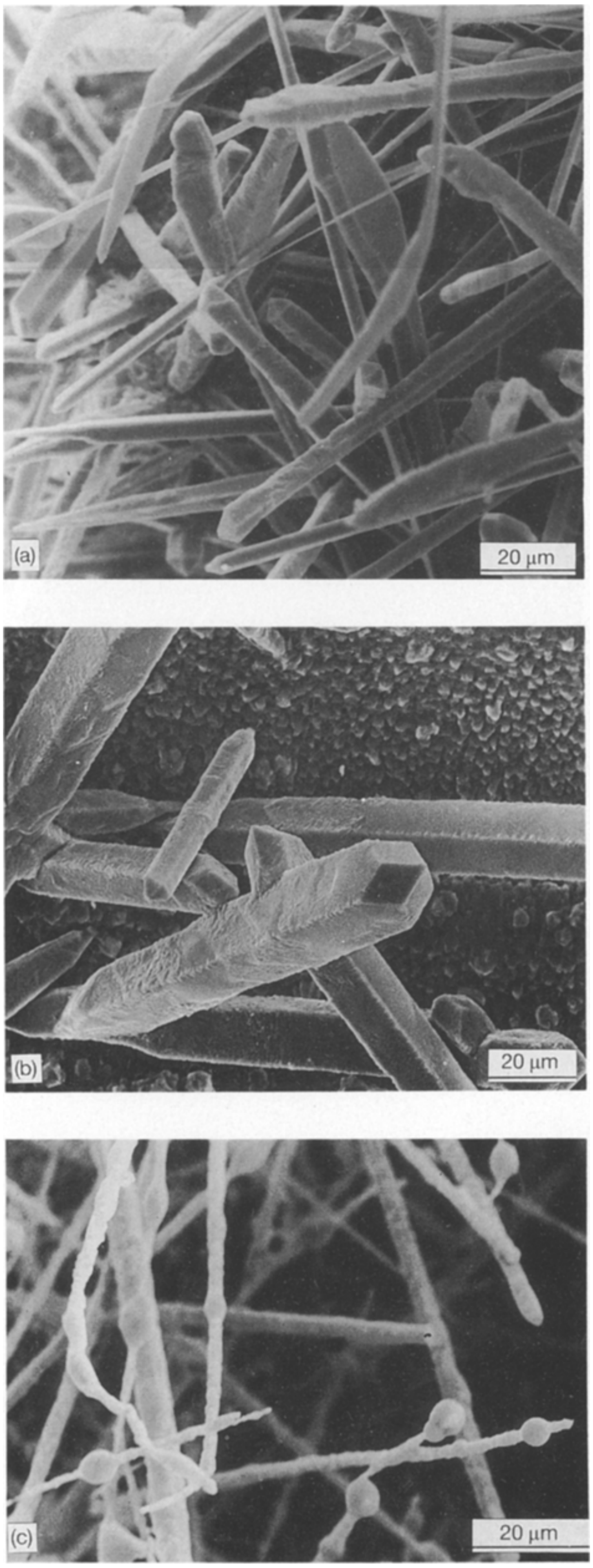

Figure 3 CdO whiskers grown on CdS crystal substrates layered with Ag: (a) threads, needles, prisms and plates; (b) four-walled prisms with faceted upper ends and faulty walls; (c) spheres and sphere-like formations at the apex and along the stem of the whiskers.

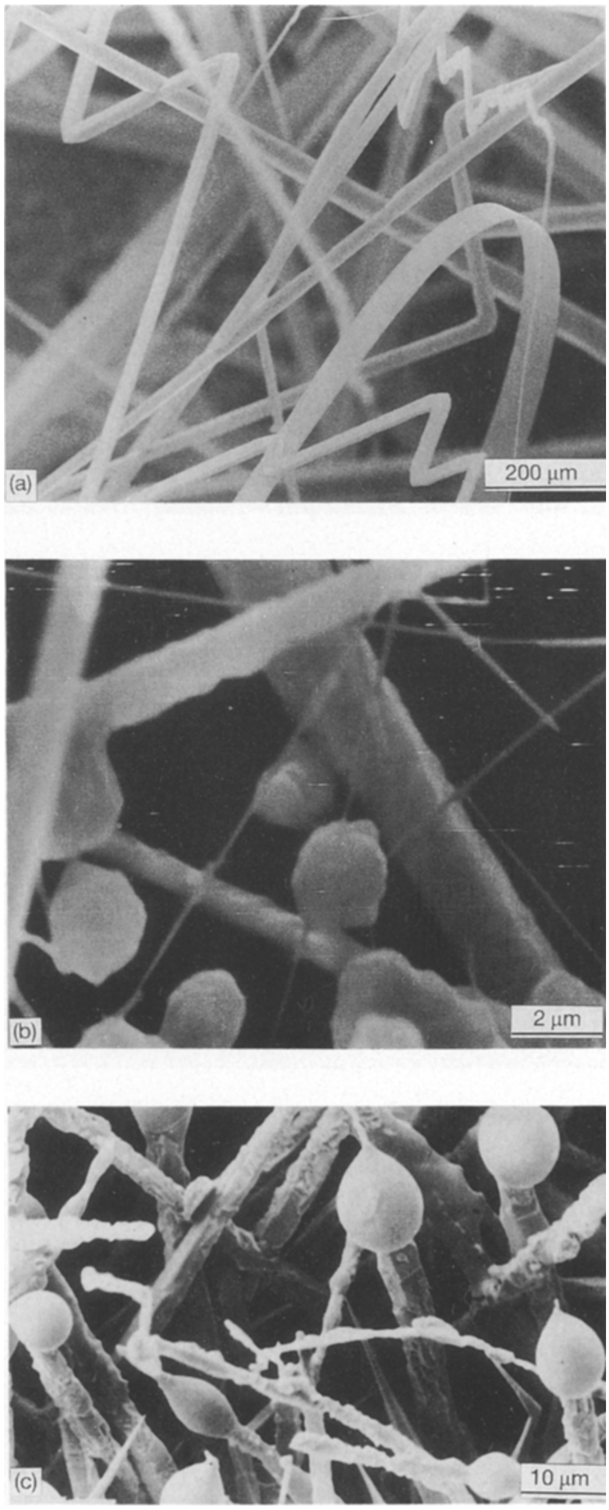

Figure 4 CdO whiskers grown on CdS crystal substrates layered with Au: (a) threads, band, bends and arc; (b) sphere-like formations along the whisker stem; (c) sphere-like formations ("drops") at the whisker apex.

However, in other cases there are significant variations, e.g. whiskers obtained with Pt as an impurity (Fig. 9) and with Ni or Pd (Figs 7 and 8). We shall next point out some typical morphological specificities of the whiskers obtained by using various impurities.

With Ag as an impurity (Fig. 3) the whiskers have typical forms of threads, needles, prisms and plates; a tendency towards regular geometrical forms, however with great deviations from these ("irregular" forms); bends, i.e. sudden changes in the direction of growth; arcs; spheres ("drops") at the whisker apex and stem, whereas in many cases the diameter of the drop is larger than the thickness of the whisker; crystal faces with numerous faults; whiskers in the form of melted

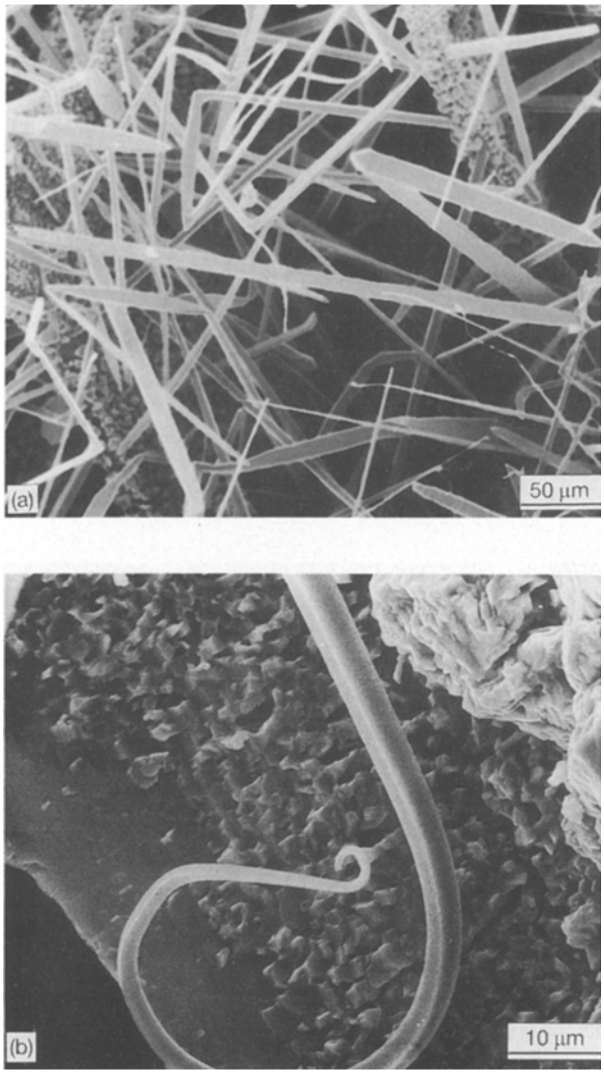

Figure 5 Whiskers grown on substrates layered with Al: (a) threads, plates and bends; (b) arc.

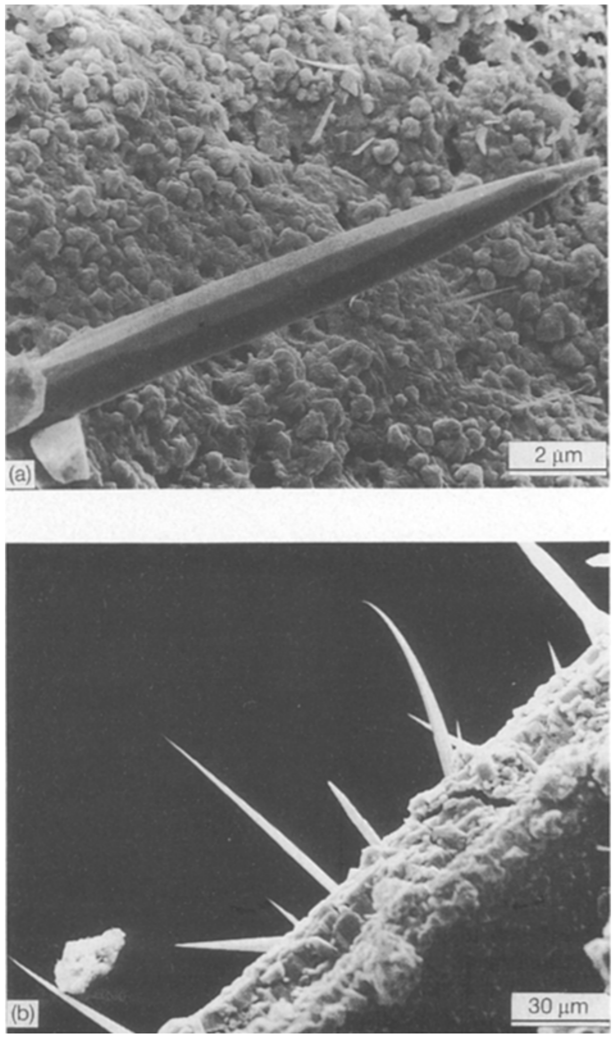

Figure 6 Whiskers grown on substrates layered with Si: (a) pencil-shaped whisker; (b) needles and arc.

and frozen formations; and whisker lengths of up to 2.5 mm.

With Au as an impurity (Fig. 4) there is a high density of whiskers; a large variety of forms–threads, prisms, plates, bands, etc.; regular geometrical forms are dominant, with mainly long and thin well-faceted smooth whiskers; a lot of bends; arcs and spirals; spheres and sphere-like formations at the apex; and whisker lengths of up to 4.5 mm. A study of the bends showed the following: there are angles of deviation which occur very frequently (32–34° and 84–90°) and angles which are very rare (about 60°), as well as angles which have a medium frequency of occurrence and vary within a wide range.*

With Al as an impurity (Fig. 5) there is a large variety of forms; considerable deviations from the regular geometrical forms; bends; arcs; and "melted and frozen" threads.

With Si as an impurity (Fig. 6) there are needles, pencil-shaped whiskers, "irregular" forms and comparatively short whiskers.

With Mn as an impurity (not presented) there are threads, prisms, "irregular" forms and arcs.

With Ni or Pd as impurities (Figs 7 and 8) there are threads, prisms, plates; thin prisms passing into wide plates with a change in the direction of growth by about 45° ("flags"); prisms with well-faceted apexes; faceted formations on the apex; regular forms, smooth walls; no arcs, spirals or spheres; no other bends, except the "flags"; comparatively short whiskers; though rare, there are some "irregular" forms, faulty facets, and "melted and frozen" whiskers.

With Pt as an impurity (Fig. 9) there are threads, prisms, needles; mainly short and thin whiskers; numerous arcs; spheres at the apex and along the length of the whiskers; and faceted formations at the apex.

3.4. Growth of whiskers on metal plates

The experiments on obtaining whiskers by the technology described above but with substrates of massive Zn or Cd, instead of CdS crystal substrates, resulted in

* What is concerned here is the angle of deviation in the direction of growth, which is additional to 180° for the bending angle. The paralactic error was avoided when measuring the bending angles.

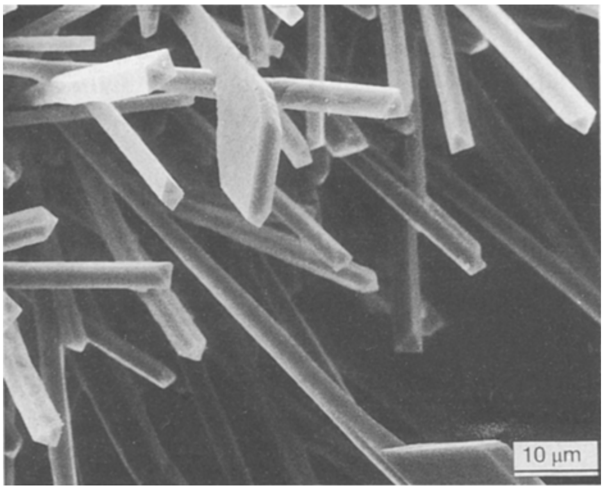

Figure 7 Whiskers grown on a substrate layered with Ni: prisms and plates.

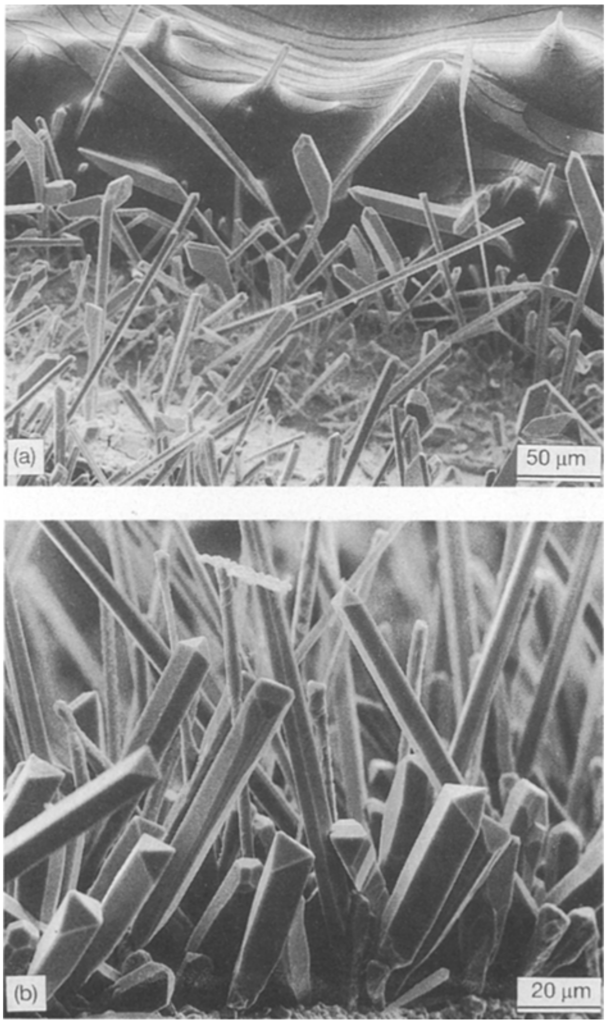

Figure 8 Whiskers grown on substrates layered with Pd: (a) prisms, plates and "flags"; (b) prisms with specific faceting of the prisms' upper ends.

positive outcomes, too (Table II).‡ In this case, however, the yield of whiskers is smaller.

This technology also requires the presence of impurity metal (a thin layer evaporated on the massive substrate, Table II) as a necessary condition for whisker growth; no whiskers grow on pure (non-layered) Zn or Cd plates treated under the same conditions.

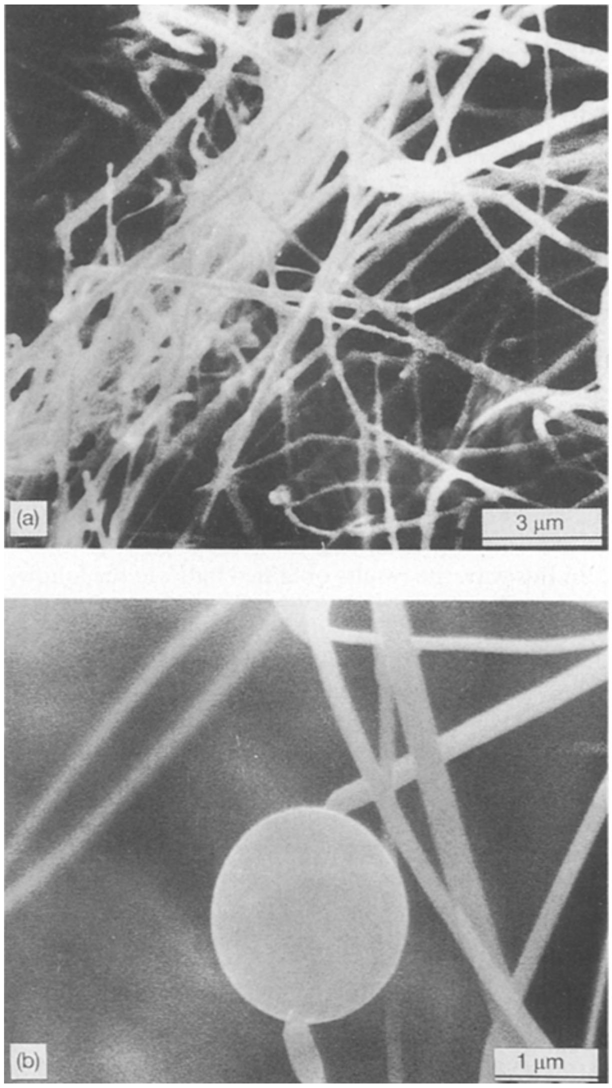

Figure 9 Whiskers grown on substrates layered with Pt: (a) very thin threads and arcs; (b) thin threads and sphere ("drop") with a diameter much larger than the thickness of the thread.

TABLE II Growth of whiskers on a massive metal substrate (Zn or Cd) coated with a thin layer of Cu, Ag, Au or Al

Substrate and coating	Whiskers obtained	Efficiency of growth
Zn, Cu	Yes	Medium
Zn, Ag	Yes	Medium
Zn, Au	Yes	Medium
Zn, Al	Yes	Medium
Cd, Cu	Yes	Poor
Cd, Ag	Yes	Medium
Cd, Au	Yes	Poor
Cd, Al	Yes	Poor

The composition of whiskers grown on metal substrates was only studied by X-ray microanalysis. The results show that the threads which have grown are probably of a CdO composition (in the case of a Cd substrate), or a ZnO composition (in the case of a Zn substrate). A study of the morphology revealed crystal

‡ These investigations are still in an initial stage and the results presented are far from final.

forms similar to those of whiskers grown on CdS substrates. Apart from this, some other specificities were observed here, too, as spacious spirals, branchings, pencil-shaped formations at the ends of bands, etc.

4. Discussion

The need to use an impurity for starting whisker growth on the surface of CdS crystals (Table I, Figs 2–9) supports the VLS mechanism of crystal growth. The same is also confirmed by the presence of spheres ("drops") on whisker apexes and stems (Figs 3c, 4b and c, 9b) and by the presence of Ag or Au in the spheres on the apex [4]. The numerous bends, as well as the fact that the direction of growth changes to a large extent arbitrarily, i.e. there are various angles within a wide range, also support the VLS mechanism of growth [8].

In this way, the results obtained indicate the following:

(a) CdO whiskers with micrometre thickness and millimetre length could be obtained by the simple technology described earlier [3], whereas not only Au may be used as an impurity, but also Ag, Al, Ni, Pd or Pt; the most efficient growth, however, is promoted by Au.

(b) Whiskers may be grown by the same technology, using Si or Mn as an impurity solvent. In these cases, the yield of whiskers is smaller and their composition has not been studied; some suggestions can be made that it is CdO.

(c) The growth of CdO whisker crystals by the proposed method is based mainly on the VLS mechanism. However, the role of another mechanism cannot be completely excluded. This is supported, for example, by the large variety of whisker crystal forms observed, even with one and the same impurity element.

The lowest temperature which allows whisker growth on CdS substrates is weakly dependent on the impurity element used, i.e. it is almost the same, about 670–680 °C for all impurities, and is considerably higher than the eutectic temperatures of the respective metal pairs (Au–Cd 308 °C, Cd–Ni 318 °C, Cd–Pd 320.4 °C, Cd–Pt 315 °C, etc: [9]). This indicates that the minimum temperature of growth is not determined by the condition for eutectic formation (as is the case for some methods of whisker growth by the VLS mechanism, e.g. [10]), but by other, higher-temperature processes, where the material of the substrate (CdS) is significant. Such processes can be, for instance:

(a) CdS decomposition ($T_{\text{dissociation}} \simeq 600$ °C [11]) and loss of S until free Cd is obtained, which then alloys with the impurity element on the substrate surface and forms the drops initiating whisker growth;

(b) occasional reduction of CdS by the impurity element, having the same result;

(c) evaporation of Cd and appearance of Cd vapour with enough density and a pressure close to atmospheric ($T_{\text{boiling}} = 765$ °C for Cd [12]) in the above-substrate space;

(d) entry of Cd vapour and oxygen molecules into the drop (cadmium-impurity liquid alloy) at the apex of the whisker and diffusion of the atoms and/or ions from the drop's free surface towards the liquid–solid (drop–whisker) boundary;

(e) oxidation of Cd in the liquid phase ($T_{\text{oxidation}} \simeq 400$–$550$ °C [9]) and deposition of CdO at the whisker apex (the impurity element may serve as catalyst of the oxidation);

(f) oxidation of Cd in the gas medium and deposition of CdO on the whisker faces.

On the other hand, the maximum temperature allowing whisker growth (about 730 °C) is obviously determined by the strong disintegration of the CdS substrates at higher temperatures and their loss of free Cd due to evaporation and oxidation; i.e. the upper limit of the temperature interval of whisker growth is also determined by the material of the substrate and is almost the same for all impurities.

The efficiency of whisker growth in the temperature interval thus determined is obviously largely dependent on the physical and chemical properties of the impurity element used at temperatures in that interval. The most important properties of the impurity, i.e. those having the strongest impact on the growth process, according to the authors, are as follows: chemical activity with respect to S and O; ability to alloy with Cd and form small drops from the alloy; catalytic activity, mainly with respect to the oxidation of Cd; and diffusion velocity in CdS. The differences in these properties in the various impurities used determine the different yields of whiskers (Table I). Obviously, the same is the reason for the variations in the forms and sizes of whiskers grown by different agents (Figs 3–9).

In conclusion, it can be summarized that the impurity element does not affect the composition and structure of whiskers grown by the technology suggested above: for all tested impurities they are of CdO and have a lattice of NaCl type. The impurity, however, significantly affects the crystal form, as well as the efficiency of whisker growth.

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