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Vaporization of CdS single crystals and formation of negative whiskers

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The mechanism and kinetics of vaporization of A^{II}–B^{VI} compounds (mainly of CdS single crystals) in hydrogen flow are studied. It is found that a liquid forming agent (gold) evaporated on the crystal surfaces significantly increases vaporization rates and tends to transfer the vaporization regime from a kinetic to a diffusion one. Formation mechanism of "negative whiskers" (crystallographically oriented cavities underneath the crystal surfaces) is investigated. It is concluded that the negative whiskers are formed under the action of the liquid phase which lowers nucleation barriers on the liquid–solid interface.

1. Introduction

Investigations on the vaporization of single crystals are not as numerous as those on growth, but nevertheless they prove substantially helpful in the studies of the mechanism and kinetics of crystallization. This is because firstly, the growth is always accompanied by elementary acts of vaporization (and in general of atom or molecule detachments), secondly, vaporization by itself provides very important information on crystallization phenomena, and lastly, vaporization (gas etching, decrystallization in general) is a substantial stage for substrate preparation prior to the growth of crystals and epitaxial films.

Of various materials, single crystals of A^{II}–B^{VI} compounds seem to be those most investigated as far as vaporization is concerned. However, there is still much to be learned about the effect of impurities on the vaporization mechanism and kinetics. In particular, most investigations using gravimetric and mass-spectrometric methods [1–8] are based on the thermodynamic approach and, consequently, cannot take into account the impurity effects. On the other hand, it has been shown [9, 10], that during ZnS single-crystal vaporization in a hydrogen flow, the impurities (non-controlled or intentionally introduced) have a decisive effect on the kinetics and mechanism of the process causing, in particular, the formation of negative whiskers (elongated channels or tunnels).

In this paper, further investigations on the vaporization of A^{II}–B^{VI} compounds (mainly of CdS) are described. The aim of the investigations is to examine the generality of the mechanism and kinetics found earlier for ZnS crystals and, in particular, to examine the formation mechanism for negative whiskers and the impurity effects in the vaporization kinetics. In addition, control experiments with ZnS crystals were carried out to elucidate the role of impurities in negative whisker formation.

2. Experimental details

2.1. Preparation of wafers

Vaporization was performed on CdS single-crystal wafers cut from a bulk crystal which was grown from vapour [11]. The typical dimensions of the wafers were $5 \times 7 \times 0.5\,\mathrm{mm}^3$. In addition, separate experiments were performed with ZnS hexagonal wafers which were cut from bulk crystals grown from the melt in a graphite crucible under high pressure of an inert gas (argon).

The CdS wafers of $\{0001\}$ orientation and those of ZnS $\{111\}$ were chemically etched prior to the experiment. The cadmium sulphide was treated in hydrochloric acid to water solution

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(proportion 1:4) at boiling point for 6 to 7 sec; in doing so, sharp hexagonal pits were formed on the Cd (0001) face while conical dislocation pits showed on the S $(000\bar{1})$ face. Zinc sulphide was etched in a similar solution (proportion 1:2) for 1 to 1.5 min; hexagonal pits again appeared on the Zn (111) face, whereas the S $(\bar{1}\bar{1}\bar{1})$ face became covered by a continuous layer of sulphur. On some of the substrates a thin (~ 300 Å) film of gold was evaporated to form a liquid phase at vaporization temperatures. At the temperature used, the gold film formed a thin liquid layer of CdS–Au alloy which was broken under surface tension into small globules, as observed morphologically by transmission and reflection optical microscopy and by scanning electron microscopy.

2.2. Experiments on vaporization

Experiments were performed in an apparatus described earlier [9, 10]. The main part is a vertical chamber heated by a resistance furnace. Hydrogen (or a $H_2 + 0.2\%$ HBr gas mixture) was passed through the chamber at a rate of 1 litre min^{-1}. Simultaneously four specimens of CdS (0001) and $(000\bar{1})$ with and without gold, as well as a specimen of CdS $(11\bar{2}0)$ were installed in the chamber; in the control experiments, ZnS (111) wafer without gold was also exposed to gas flow.

After the experiment, vaporization rates were determined by weight-loss measurement and the morphology of the vaporized surfaces was examined with the aid of an optical microscope in reflected and transmitted light with Nomarski interference contrast and with a scanning electron microscope.

3. Results and discussion

3.1. Vaporization rates

The temperature dependencies of vaporization rates of different faces (with and without gold coating) are plotted in Arrhenius co-ordinates in Fig. 1. Analysis of these results revealed the following:

(a) the vaporization rates of the Cd (0001) and S $(000\bar{1})$ faces are practically the same over the whole temperature interval, according to our earlier results [9];

(b) the gold film that forms a liquid phase with CdS at temperatures above 600° C (as seen from the morphology), substantially accelerates vaporization. For instance, at 650° C, the vaporization of the gold-coated wafers accelerates about 5 to 6 times;

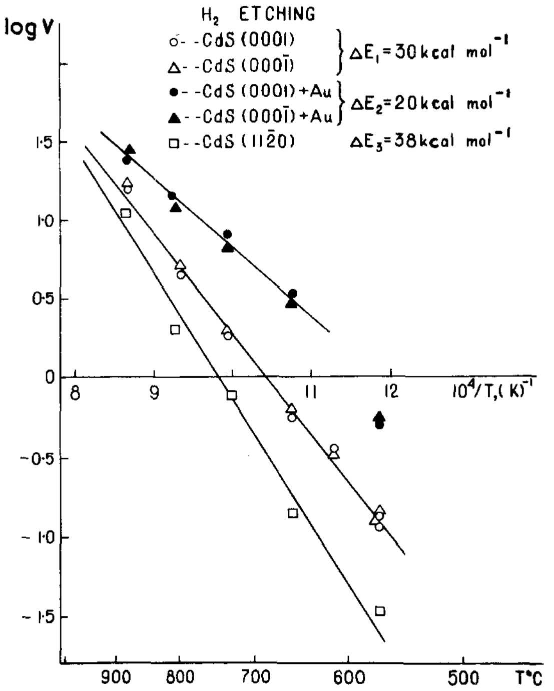

Figure 1 The temperature dependence of varporization rates in hydrogen of different faces of CdS (with and without gold).

(c) the activation energies are approximately the same for the polar faces of CdS and are ~ 30 kcal mol^{-1} without and ~ 20 kcal mol^{-1} with gold, respectively;

(d) the experimental data on the gold-coated specimens at a temperature of about 570° C show some departure from the general dependence; however, the vaporization rate of gold-coated specimens again accelerates about 5 to 6 times;

(e) at temperatures of ~ 900° C the vaporization rates for all CdS specimens are practically the same;

(f) the vaporization rates of the $(11\bar{2}0)$ face at temperatures as high as ~ 800° C are 2 to 3 times less than those of the {0001} faces (without gold). Such a "stability" may be associated with the electrical neutrality of the $(11\bar{2}0)$ face, as noted earlier in respect of its analogue – the {110} face in a sphalerite structure [12].

Results (b) and (c) are in a qualitative agreement with Wagner and Ellis's data on the vapour–liquid–solid growth of silicon by means of gold [13], with Lou and Somorjai's data on GaAs vaporization with gallium and tin [14], and also with our earlier data on ZnS vaporization with and without gold [9]. These results allow us to arrive at a conclusion regarding vaporization regimes. The

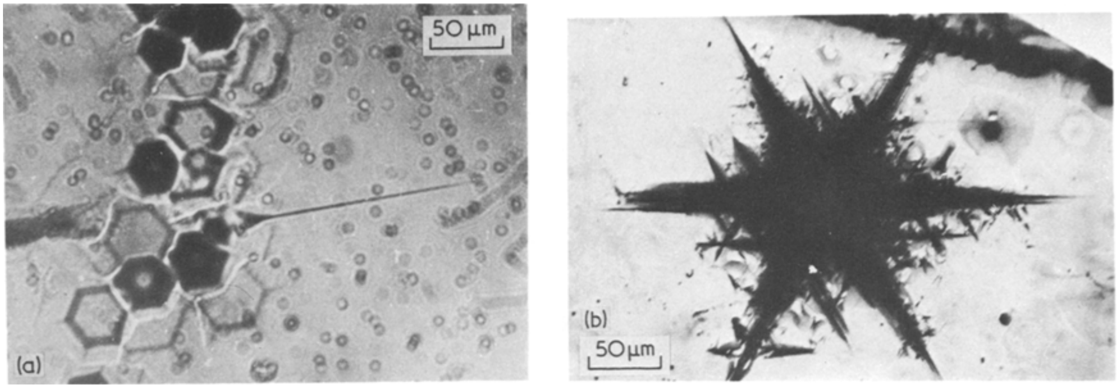

Figure 2 Vaporization features; negative whiskers in CdS single crystal of (0001) orientation. The temperature of the process is 707° C, the medium is hydrogen, the duration, 30 min. Optical micrographs of the varporized surfaces in transmitted light.

significant differences in the vaporization rates with and without gold at low temperatures and the convergence of the rates at high temperatures suggest that the kinetic regimes operate at low temperatures for uncoated specimens whereas the liquid phase tends to transfer the regime from a kinetic to a diffusion one. In addition, when the temperature rises, a transition from the kinetic to the diffusion regime begins as is confirmed by morphological data (see below).

3.2. Morphology

3.2.1. The Cds (0001) face: negative whiskers

Earlier [10], negative whiskers were observed in single crystals during vaporization of ZnS. These vaporization features are crystallographically orientated cavities underneath the crystal surface. Here, quite similar features were observed at CdS crystal vaporization in hydrogen: they were formed at temperatures of ~ 660 to 780° C. Typical micrographs of the vaporized surfaces are shown in Fig. 2a and b. In accordance with Givargizov and Babasian [10], negative whiskers were observed primarily on Cd(0001), e.g. on a "metal face" the density of the features being, however, less than on ZnS crystals (it should be noted that ZnS crystals were grown from the melt at high temperatures, whereas the CdS crystals were grown from the vapour at relatively low temperatures). Also in accordance with Givargizov and Babasian [10], negative whiskers were typically formed from the edge of the specimens (Fig. 3).

Earlier, a conclusion was drawn about the importance of liquid-forming impurities in the generation of negative whiskers. Here, this has been proved directly by experiments with impurities. If CdS wafers are coated with a thin film of gold (~ 300 Å), the formation of negative whiskers is dramatically intensified (Fig. 4a). The

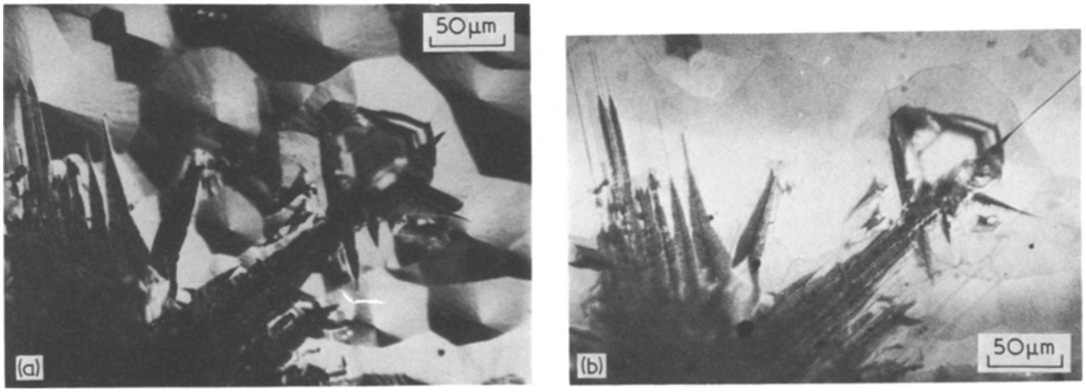

Figure 3 The negative whiskers formed on the CdS (0001) face of the substrate edge, (a) in reflected light of the microscope, (b) the same region in transmitted light.

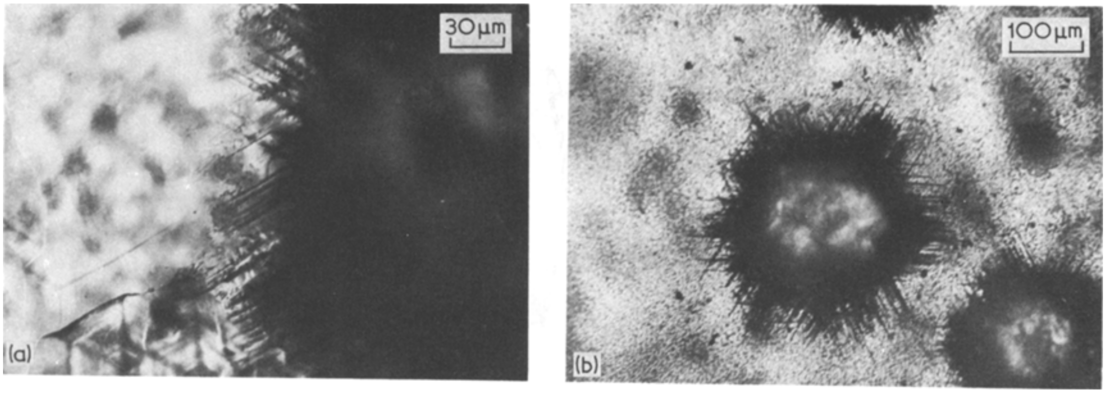

Figure 4 The initiation of negative whiskers with the aid of gold forming the liquid phase with the crystal at high temperatures: (a) the CdS crystal; the dark area to the right is a pit associated with a gold spot evaporated through a mask; negative whiskers grown from that spot; (b) the ZnS crystal: S ($\bar{1}\bar{1}\bar{1}$) face, spots and negative whiskers are associated with incorporated gold particles.

control experiment with ZnS has shown an analogous result (Fig. 4b).

A more detailed analysis of the negative whisker morphology makes it possible to draw some conclusions regarding the formation mechanism of such features. Fig. 5 shows an SEM of a six-spike "star" on the CdS surface. Analysis of this micrograph, together with Figs. 2b and 3b, suggests that the formation of very narrow channels is characteristic of CdS, the channels having an almost permanent cross-section and rather an abrupt transition to the broadening base. Such a form is probably due to the relatively low temperature of the process, the two parts of the negative crystal being associated with different mechanisms of formation: the narrow channel is formed by the solid–liquid–vapour (SLV) mechanism, while the broadening base is formed by the solid–vapour (SV) mechanism. This phenomenon is analogous to that in whisker growth: at relatively low temperatures whiskers grow in the form of prisms (or cylinders), while at higher temperatures, owing to the vapour–solid mechanism [15] they take the form of more or less blunt whiskers.*

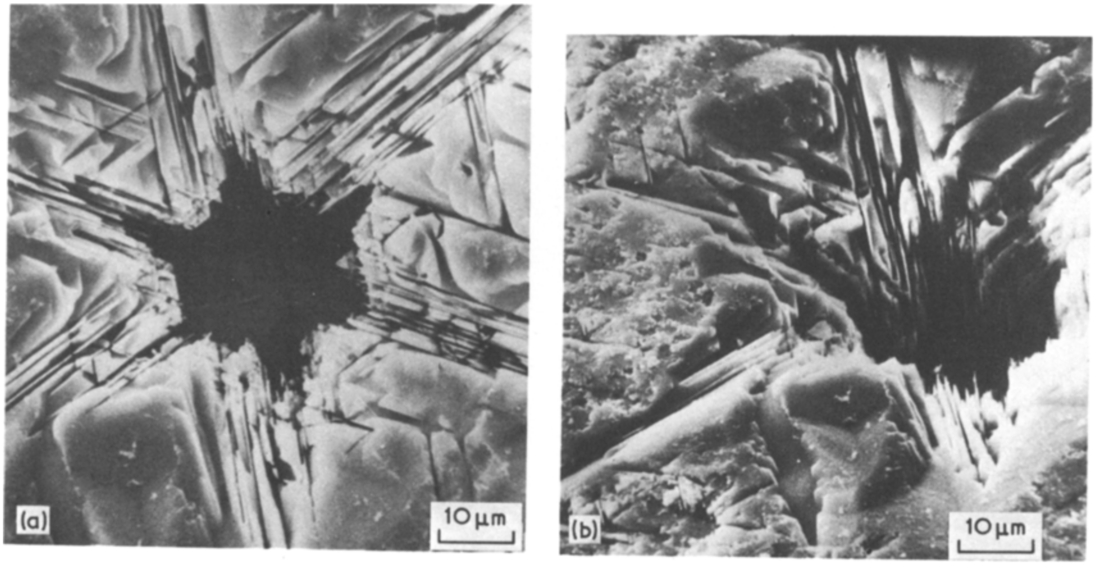

Figure 5 SEMs of a "star" (vaporization feature): (a) at small magnification scanning angle 0°; (b) the same "star", the initial areas of negative whiskers, scanning angle, 45°.

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*It should be noted that the liquid phase contributes to the growth of positive whiskers both at low and high temperatures; the contribution, however, is far less at relatively high temperatures so that rather blunt whiskers are formed here.

The rough surface (in this case, with negative whiskers as a characteristic element of the relief) is usually attributed to the kinetic regime of the process [16]. At a temperature $\gtrsim 830°$ C, the surfaces become smooth, a fact which is an indication of the diffusion regime of vaporization. In experiments with $H_2 + HBr$ mixtures, the smoothness was observed at as low a temperature as $\sim 730°$ C. This seems to be due to the ability of HBr to interact chemically both with cadmium and sulphur with formation of H_2S and $CdBr_2$ (in H_2, only sulphur interacts with hydrogen chemically, while Cd is evaporated physically). Such a change in the morphology agrees with the data on vaporization rates (see below).

3.2.3. S (000$\bar{1}$) face: columnar structures

At relatively low temperatures ($\lesssim 830°$ C), the S (000$\bar{1}$) face showed a rather rough surface after vaporization in hydrogen – a fact which is indicative of the kinetic regime of vaporization. Typical micrographs of such surfaces are shown in Fig. 6. In some regions columnar structures were formed. Earlier, a similar morphology was observed on the Se (0001) face of CdS crystals [9]. There, it was explained by a poison effect of the impurities of an oxide nature; here, a similar mechanism may be operative.

At high temperatures, the vaporization surfaces treated with hydrogen appeared smooth, which is an indication of the beginning of the transition to the diffusion regime. At vaporization of CdS in an $H_2 + HBr$ mixture the smooth surface characteristic of the diffusion regime was observed on this face starting with temperatures of $\sim 730°$ C.

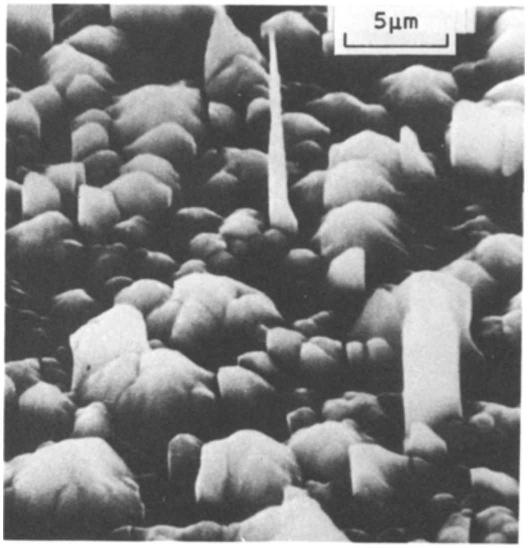

Figure 6 Micromorphology of the S (000$\bar{1}$) face; SEMs, scanning angle, 45°.

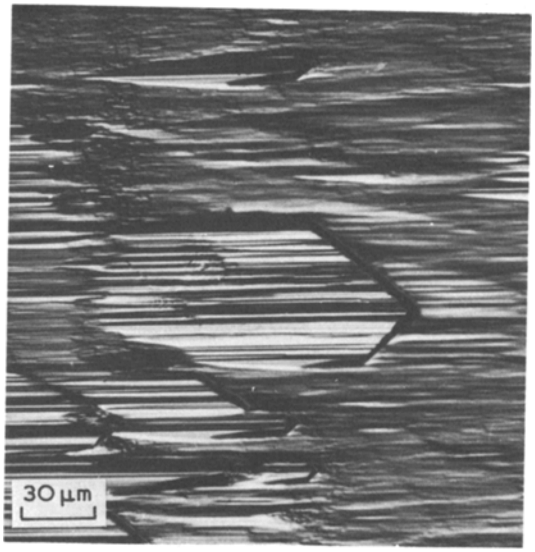

Figure 7 Optical micrograph of the (11$\bar{2}$0) face.

3.2.4. (11$\bar{2}$0) face

For this face, a step-chain structure was characteristic (Fig. 7), such a morphology being preserved up to 950° C.

4. Conclusions

(1) During CdS single-crystal vaporization in a hydrogen flow at temperatures of 580 to 780° C, specific features – negative whiskers – are formed on basal faces {0001}, in accordance with earlier observations for ZnS crystals.

(2) In experiments where surfaces are coated with a thin gold film as a liquid-forming impurity, a model of negative whisker formation by a solid–liquid–vapour mechanism, assumed previously for ZnS vaporization, applies.

(3) The liquid phase formed on the surfaces by the gold film is able (at relatively low temperatures to accelerate the vaporization rate substantially.

(4) Comparison of the morphological and kinetic data on the vaporization specimen without metal coating shows that a transition from a kinetic to a diffusion regime takes place when the temperature rises, the transition temperature depending both on crystallographic orientation and on gas-phase environments.

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