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TRANSMISSION ELECTRON MICROSCOPIC STUDY OF ANTI-PHASE BOUNDARIES (APB) IN ZINC OXIDE WHISKERS

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In the present paper it is shown that in the case of rapid growth of ZnO whiskers out of the gaseous phase from highly supersatmed pairs, antiphase boundaries may be formed. It was shown that near the sublimation temperature of zinc oxide the system of parallel antiphase boundaries along $[\bar{1}011]$ becomes split, forming a system of intersecting antiphase boundaries running along the $[10\bar{1}1]$ and $[10\bar{1}\bar{1}]$ directions.

Models by means of which the mechanism of antiphase boundary movement is explained are given in the paper.

1. Introduction

The growth of crystals from the gaseous state under conditions far removed from thermodynamic equilibrium gives rise to the possibility of formation of various kinds of lattice defects. One of the more common defects in such crystals is the occurrence of antiphase boundaries.

Antiphase boundaries are surface along which a change in atomic configuration occurs within the same crystal lattice. They are formed as a result of the displacement of certain sections of the lattice in a direction perpendicular to the defect surface [1]. The region contained within the antiphase boundaries is termed an antiphase domain. The structure of a single domain is described by means of a constant displacement vector R.

The best method for observing the microregions occupied by the domains is by use of electron microscopy and selective electron diffraction. There also exist papers [4, 5] from which it appears that antiphase domains can also be observed by applying chemical etching techniques.

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Holt [6] has studied the possibility of antiphase boundary occurrence in semiconductor-compound crystals of the $A^{II} B^{IV}$ type, possessing a sphalerite structure. In such crystals antiphase boundaries form between the (111) *A* and $(\bar{1}\bar{1}\bar{1})$ *B* faces. Assuming that for compounds of the group $A^{II} B^{IV}$, *i. e.* of sphalerite and wurtzite structures, the *A* and *B* atoms possess bonds in a tetrahedral configuration Sp^3, it is to be expected that all atoms on both sides of a APB are of the same kind. According to [5, 6], this type of bonding of identical atoms along APB is infavoured and possesses a higher energy than direct bonding (*AB*-type).

2. *Experimental*

2.1. Method of obtaining ZnO whiskers

The synthesis of ZnO whiskers which are the object of interest in this paper was based on the results of Dadson and Savage [7]. The method is based on a two-step procedure for conducting the process.

In the first step, reduction of polycrystalline ZnO by hydrogen takes place at a temperature of about 1350°C.

$$ZnO_{(s)} + H_{2(g)} \rightarrow Zn_{(g)} + H_2O_{(g)}$$

Subsequently, after displacement of the zinc pairs through a stream of nitrogen into the oxidising region, the reaction

$$Zn_{(g)} + 1/2\ O_{2(g)} \rightarrow ZnO_{(g)}$$

Fig. 1. ZnO whiskers obtained from the gaseous phase

takes place, together with condensation of the ZnO pairs on the walls of the reaction vessel.

The rate of hydrogen transfer through the system was 40 cm^3/min, the rate of oxygen flow 50 cm^3/min, and the rate of nitrogen flow was 500 cm^3/min.

The whiskers obtained were in the form of thin needles of a 10^{-3} to 10^{-5} mm diameter and a length of 2 to 20 mm.

Fig. 1 presents a collection of the ZnO whiskers obtained.

A detailed description of the method for obtaining whiskers and crystals of ZnO in the way described is given in Ref. [8].

2.2. Antiphase boundary structure in ZnO whiskers

Fig. 2 depicts a system of parallel lines running along the [$\bar{1}011$] direction. The distance between them is around 330 Å. In certain places a line system such as that shown in Fig. 2b was observed. The total length of such lines in a unit volume of whisker is around 4×10^{10} cm/cm^3.

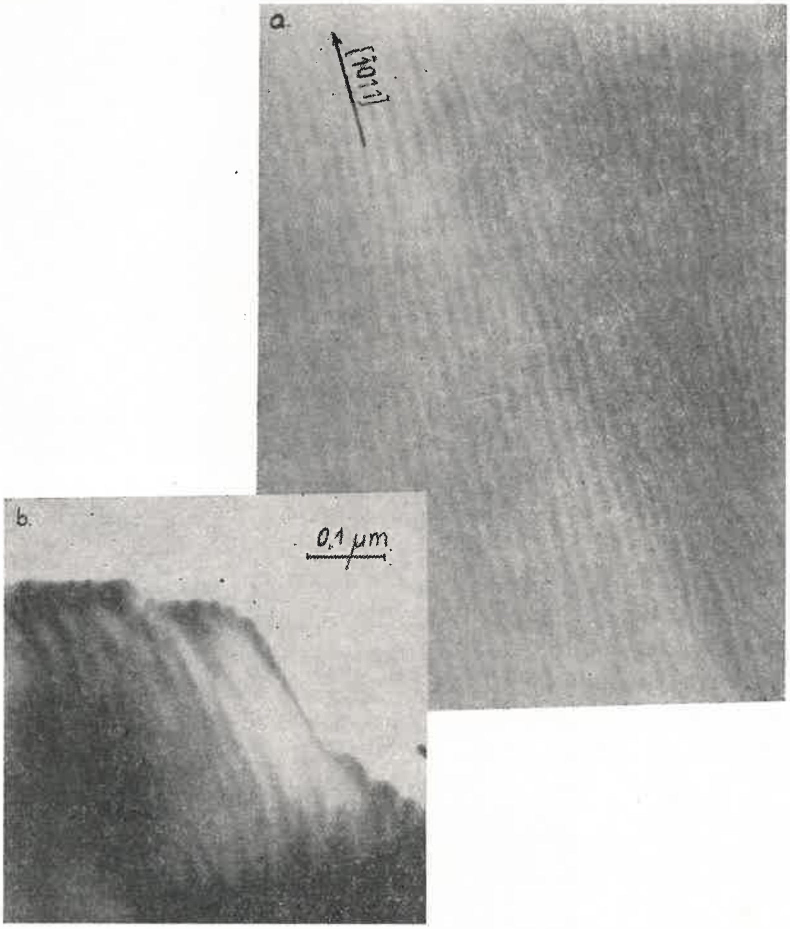

Fig. 2. System of antiphase boundaries in ZnO whiskers, $g = (0\bar{1}10)$

The electronogram taken of the structure shown in Fig. 2a is presented in Fig. 3b. Fig. 3a shows, on the other hand, the electronogram of a whisker of ZnO which does not exhibit this type of defect. This corresponds to zinc oxide, which crystallizes into a wurtzite-type structure. The orientation of lines was carried out on the basis of the electronogram shown in Fig. 3b.

Comparing the electronograms of Fig. 3 it can be surmised that the additional reflexes observed in Fig. 3b in the nature of a superstructure are the result of the existence of latttice defects. The appearance of additional reflexes may be largely connected with the existence of new crystalline phases, twinning [1], or with antiphase boundaries [6].

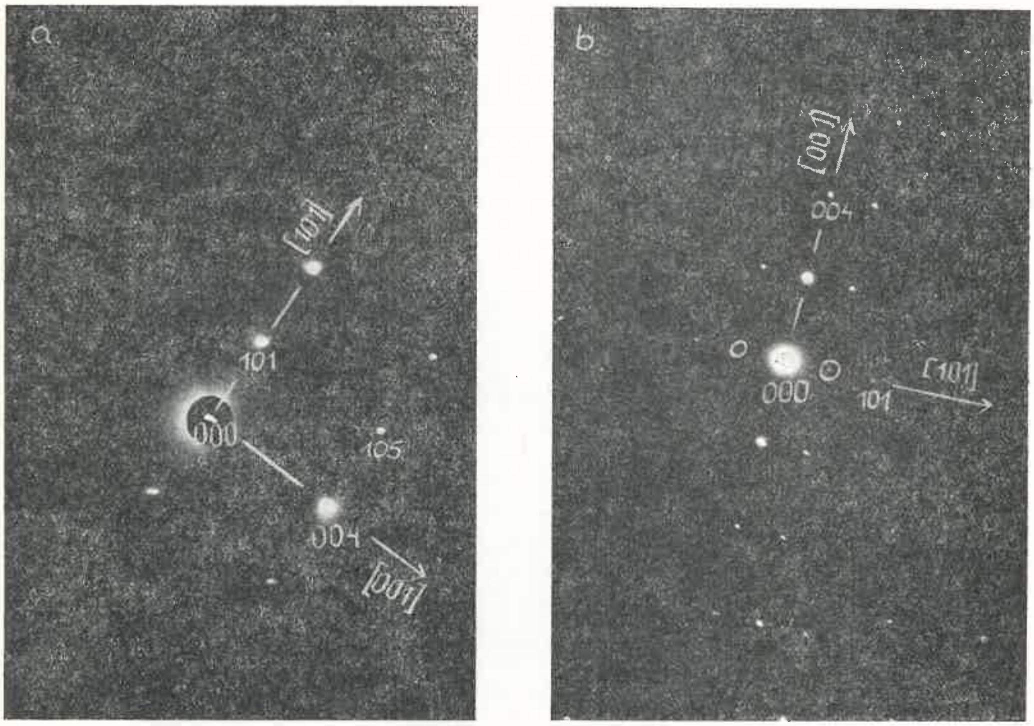

Fig. 3. Electronogram of ZnO whiskers: a) taken for an undefective whisker, b) taken for a whisker containing antiphase boundaries

It seems that this type of defect may be ascribed to antiphase boundaries. A detailed analysis of the results follows in the text.

In Fig. 2 one can observe that the contrast of lines is relatively rather diffuse. This effect can be explained on the basis of kinetic theory of image contrast, analysing changes in the scattering amplitude of the electron wave as a function of the depth of location of the defect at the bottom surface of the crystal [1].

$$\psi_g = \frac{i\pi}{\xi g}\int_0^t \exp(-i\alpha)\exp(-2\pi isz)dz$$

where: $\alpha = 2\pi gR = \text{const}$, s = deviation from the reflecting position, z = distance of defect from bottom surface of the foil, t = crystal thickness, ξ_g = extinction distance.

In a case where the defect is close to the foil surface, and the thickness t decrease, he contrast is diffused [9] and is reminiscent of the contrast of surface inhomogeneity.

2.3. Geometry of antiphase boundaries in whiskers of ZnO

In Holt's model [6], the antiphase boundaries in crystals of a sphalerite structure are found, through interchange of atoms A and B within the lattice in a (111) plane. Similarly, in crystals of a wurtzite structure an interchange of atoms A and B in the (0001) face of the crystal lattice should occur. In this case atom A with coordinates (000) should replace atom B with coordinates (00u) where $u \approx 3/8$ [10]. By the same token, exchange of atomic factors f_A and f_B should take place in the structural factor $F(hkl)$.

Figure 4 depicts a model of antiphase boundary formation in ZnO whiskers. It differs from the model considered by Holt and that given above for wurtzite structures in that at APB, interchange of atoms A and B does not occur, rather a change takes place in the filling of tetrahedral gaps by atoms A in a close-packed sublattice B.

It is a known fact that in a wurtzite structure in a close-packed sublattice B there exist two tetrahedral gaps. If atoms A are packed in these empty tetrahedral spaces, then the wurtzite lattice is rotated about an axis perpendicular to plane APB in this part of the crystal, while the surface of contact of atoms A of the same kind will form an antiphase boundary.

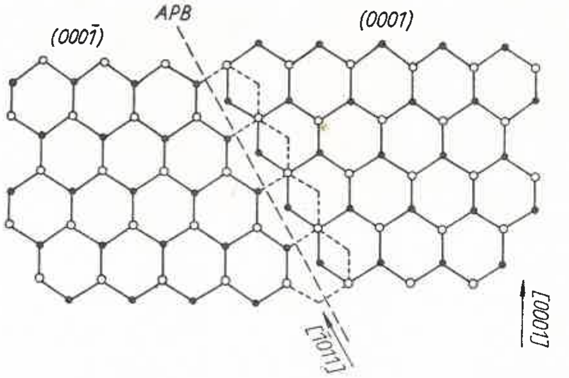

Fig. 4. Model of antiphase boundary formation in ZnO whiskers

The vector displacement of atoms A from the occupied tetrahedral gaps to empty one is equal to $1/2\langle 10\bar{1}1\rangle$. According to Drum [11], the magnitude of this vector is $3/2p + 1/2c$, where $p = 1/3\langle 10\bar{1}0\rangle$ and $c = \langle 0001\rangle$. It is to be expected that the location vectors of atoms A, (r_A), in the unit cell are shifted in the direction of the a axis by $1/2\ [10\bar{1}0]$ and in the direction of the c axis also by $1/2\ [0001]$.

The calculated values of the phase factor for various R and g vectors have been collected in Table I. The contrast upon location-error-type defects in ZnO appears whenever α equals $\pm\pi$.

TABLE I

Principal values of the phase factor $\alpha = 2\pi gR$ for various g and R in ZnO. Fault contrast is expected with $\alpha \neq$ integer times 2π

$2\pi g$	R			
	1/2 $[\bar{1}011]$	1/2 $[10\bar{1}1]$	1/2 $[10\bar{1}\bar{1}]$	1/2 $[\bar{1}01\bar{1}]$
$2\pi(0\bar{1}10)$	$+\pi$	$-\pi$	$-\pi$	$+\pi$
$2\pi(01\bar{1}0)$	$-\pi$	$+\pi$	$+\pi$	$-\pi$
$2\pi(10\bar{1}0)$	$-\pi$	$+\pi$	$+\pi$	$-\pi$
$2\pi(0002)$	$+2\pi$	$+2\pi$	-2π	-2π

If $R = 1/2\ [\bar{1}011]$ and $g = (0\bar{1}10)$, then $\alpha = 2\pi gR = +\pi$.

According to Drum [11] this means that the contrast comes from extrinsic faults, *i. e.*, those created as a result of condensation of interstitial atoms. The model presented in Fig. 4 shows that indeed the antiphase boundaries in ZnO could form as a result of the condensation of zinc atoms.

A similar model of antiphase boundary formation was considered by Phakey [12] in alexandrite $Al_{2-x}Cr_xBeO_4$. He showed that APB arise through faulty positioning of cations in the same oxygen sublattice.

2.4. Systems of intersecting antiphase boundaries in ZnO whiskers

During prolonged bombardment of the ZnO whisker surface with an electron beam, one can observe, at the moment of the crystal's sublimation, a slow movement of parallel antiphase boundaries. As a result of the process occurring, there appears a new system of lines running along the $[10\bar{1}1]$ and $[10\bar{1}\bar{1}]$ directions. The angle contained between two intersecting lines is about 62°. Computed from a stereographic projection of $[10\bar{1}1]$ and $[10\bar{1}\bar{1}]$ directions it is 58°.

Fig. 5 shows a system of intersecting lines in a bright (a) and dark (b+c) field, at an accelerating voltage of 120 kV. The electronogram taken for this structure is identical to the electronogram taken for the structure shown in Fig. 2a.

The reflexes in which pictures have been taken on a dark field have been marked in figure 5d. The line contrast of reflex (b) was changed from bright to dark.

Each line running in the $[10\bar{1}\bar{1}]$ direction begins and ends on a "lattice point" on lines in the $[10\bar{1}1]$ direction.

A contrast giving the illusion of lattice points can be caused as a result of emergence of lattice defects at the points of intersection of the antiphase boundaries.

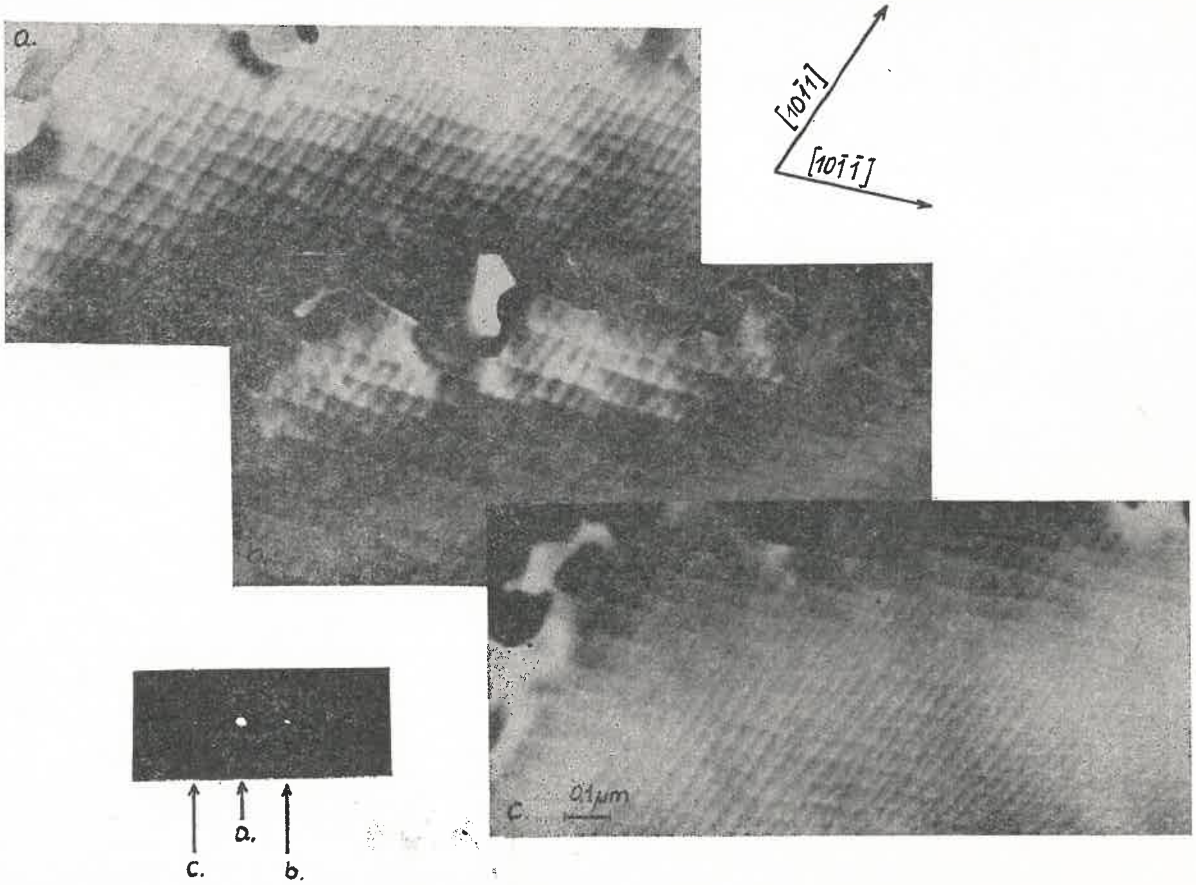

Fig. 5. System of intersecting antiphase boundaries in ZnO whiskers — $g = (0\bar{1}10)$. Prints b and c were taken in a dark field for reflexes underscored on the electronogram (Fig. 3b) and presented in Fig. d

2.5. Geometry of intersecting antiphase boundaries in ZnO whiskers

A model of intersecting antiphase boundaries is shown in Fig. 6. It was formed as a result of a shifting of zinc atoms in the tetrahedral gaps. As a result of such a change in the position of zinc atoms there also occurs a rotation of the crystallographic axis *c*.

In order to understand the mechanism of formation of intersecting antiphase boundaries we shall make use of the model shown in Fig. 7. The large white circles denote *B* atoms (oxygen), small circles denote *A* atoms (zinc) occupying the tetrahedral gaps. Empty spaces marked by numerals 1 and 2 denote unoccupied tetrahedral gaps. Antiphase bound-

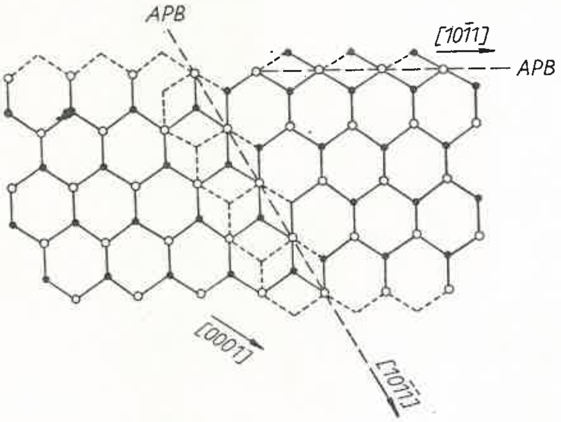

Fig. 6. Model of intersecting antiphase-boundary formation in ZnO whiskers

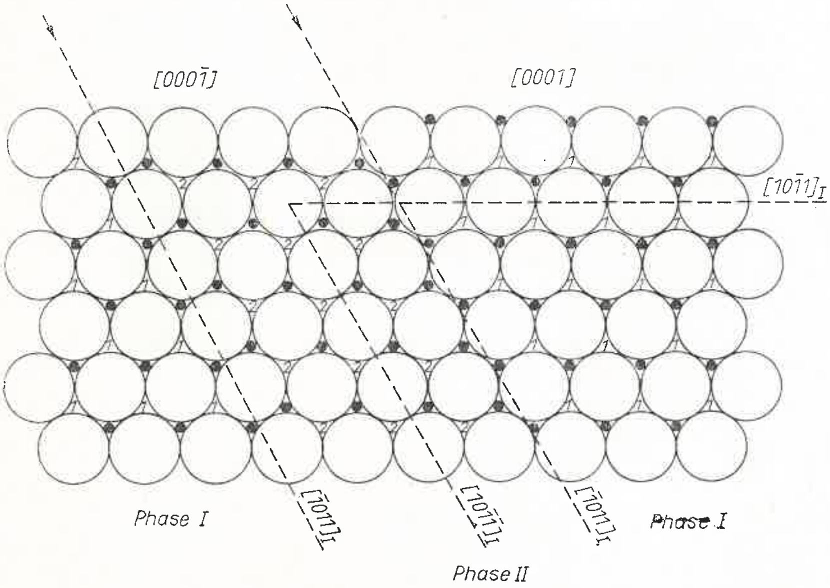

Fig. 7. Schematic diagram of coexistence of two hexagonal phases of ZnO

aries are marked by dotted lines. Motions of antiphase boundaries can take place in this model through simultaneous motions of the atoms in the oxygen sublattice. Transitions of zinc atoms in the hexagonal lattice (marked by I in Fig. 7), from locations marked by black circles can only take place to sites marked as (1). Such a transition of Zn atoms leads to the formation of a new hexagonal reciprocal lattice (marked II on Fig. 7). Transition of Zn atoms in the hexagonal lattice II takes place from sites marked by black circles in the diagram to sites marked as 2. Such a transition gives rise to phase I.

In a model thus construed the motion of antiphase boundaries can take place by way of successive jumps of Zn atoms from one tetrahedral site to another empty tetrahedral site. As a result of such jumps of Zn atoms new intersecting antiphase boundaries arise. Electronograms of the structure of a parallel-face system and of an intersecting-face system should not differ — as was indeed confirmed by direct observation.

2.6. Conditions for formation of additional reflexes of the superstructure type

Now that we are familiar with models of formation of parallel and intersecting antiphase boundaries in ZnO whiskers, let us proceed to an explanation of the causes for the formation of additional reflexes on the electronogram near the APB boundary (Fig. 8).

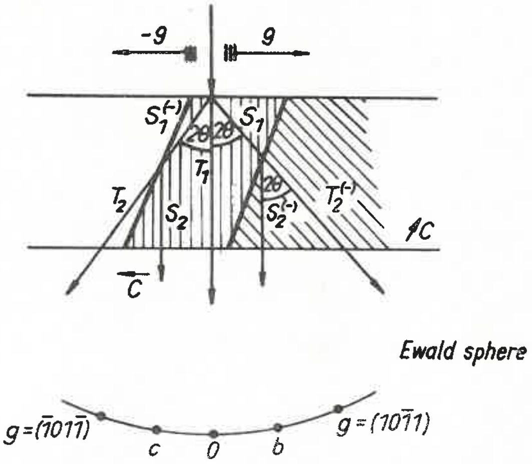

Fig. 8. Illustration of formation of additional reflexes of the superstructure type of an electronogram, near the antiphase boundary

The condition for the occurrence of double diffraction of scattered rays is that the angles between the transmitted beam T_1 and the scattered beam S_1 and the transmitted beam T_2 and the scattered beam S_2 should be equal to 2θ. This type of condition is satisfied when a local rotation of the lattice by an angle 2θ takes place. The rotation of the lattice is shown on the figure as a change in the direction of the axis c.

Double diffraction of the scattered beam S_1 leads to the occurrence of added reflexes of the superstructure type together with a phase change in beams T_2 and S_2.

Photographs taken with a dark field of superstructure-type reflexes in positions *b* should lead to a change in line contrast. Photographs taken of a superstructure-type reflex in location *c* should not give rise to changes in contrast.

This type of behaviour was in fact confirmed by direct observation.

2.7. Positioning of atomic planes in the region APB

If one designates the position of zinc and oxygen atoms in the wurtzite structure as: [10]

$$A\alpha B\beta A\alpha B\beta \ldots$$

and the reciprocal wurtzite structure as

$$\alpha' A\beta' B\alpha' A\beta' \ldots$$

then the location of zinc and oxygen atoms in the layers of a real ZnO structure can be represented as:

domain wall domain wall

| | | |

$A\alpha B\beta A\alpha\ \beta' B\alpha' A\beta' B\alpha' A\beta'\ B\alpha' \beta A\alpha B\beta \ldots$

↑ domain ↑

antiphase boundary antiphase boundary

Comparing the results of the research presented with these of Sharma [13], who showed that superdislocations with a Burger's vector equal to 480 Å can occur in ZnO whiskers, one may suspect that regions of new phase between antiphase boundaries may be treated as superdislocations with a large Burger's vector equal to the domain width. It seems that both approaches lead to the same final conclusions.

3. Conclusions

It was shown in the present work that in the case of rapid growth of ZnO whiskers out of the gaseous phase from highly supersatmed pairs, antiphase boundaries may be formed. They arise as a result of the superposition of two hexagonal planes I and II differing between them in the positioning of zinc atoms in tetrahedral gaps 1 and 2. It was shown that near the sublimation temperature of zinc oxide the system of parallel antiphase boundaries along [$\bar{1}011$] becomes split, forming a system of intersecting antiphase boundaries running along the [$10\bar{1}1$] and [$10\bar{1}\bar{1}$] directions. Electronograms taken for both systems of defects were the same.

Models by means of which the mechanism of antiphase boundary movement is explained are given in the paper.

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