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METALLIC SURFACES AND FILMS

Oscillating Character of the Diffusion of Point Defects in the Elastic-Strain Field Induced by Machining of InAs Surface

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The (100) single-crystalline InAs substrates 150–400 μm in thickness are investigated. The process of time relaxation of the point defects system formed as a result of machining of the surface of the plates is studied using X-ray techniques. An explanation is proposed for the oscillating character of the diffusion of defects in the course of stress relaxation in substrates and the role of stress concentrators in these processes.

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1. INTRODUCTION

The phenomena of instability of the physical parameters of single crystals caused by various technological workings are studied in [1–3]. In particular, the oscillating character of the behaviour of optical properties and stoichiometry at the working surface of GaAs plates after grinding of their rear face (long-range effect) is established in [1]. The wave-like character of the relaxation process in the course of plastic deformation of metals is also indicated in [4]. However, though a crucial role of the transformations in the system of point defects and impurities in the behaviour of physical properties of crystals is specified in these papers, the mechanism of positive feedback remains unknown.

Interest in the study of the effect of machining (cutting, grinding) on the properties of crystals is caused by its wide application in the production process of substrates. Therefore, the purpose of the present paper consists in the explanation of the oscillating character of diffusion in the course of elastic stresses relaxation in machined InAs crystals and also in finding out the role of intrinsic and introduced point defects and impurities in these processes.

2. THEORY

Description of the deformation processes in crystals under external actions includes the problems of nucleation of defects of various types in local deformation zones (stress concentrators) and their evolution under the action of external forces. An assumption on the formation in a crystal of the highly-excited states not concerned with phonons constitutes the basis for the model describing the behaviour of a crystal under the conditions of strong external actions [5]. These states by their nature are far from the equilibrium with a structure not characteristic of the basic state of a crystal, and their stability is maintained by external action.

Under the action of stress σ, the strain energy per one atom in the zone of stress concentrator increases by the value

$$E = \sigma^2/(2Cn), \tag{1}$$

where C is a modulus of elasticity, n is a number of atoms per unit volume.

Transition of a crystal into highly-excited state means the increase of the energy of chemical interaction of N_h atoms in the vicinity of a stress concentrator, that results in changing short-range order of the atoms arrangement. Then, the total increase of energy of the specified number of atoms is equal to $E_{hc} = N_h E_h$, where E_{hc} is the energy per one excited atom. The most probable value of N_h can be found from the condition of the maximum value of W

$$W = N!/\{N_h!(N - N_h)!\}$$

with the conservation of E_{hc}. Here W is the number of different configurations of the arrangements of N_h exited atoms taken from N configurations.

Further, according to [6], we introduce the quantity η, which has the meaning of the probability of occupation of the highly-excited state with the energy E_h or concentration of these atoms:

$$\eta = N_h/N = \exp\left(-\frac{1}{x^2}\right)\left[1 + \exp\left(-\frac{1}{x^2}\right)\right], \tag{2}$$

$$x = \sigma/\sigma_t, \quad \sigma_t = (2CnE_h)^{1/2}. \tag{3}$$

E_h is equal in order of magnitude to the difference in energy between two crystalline structures of the crystal. Its value can be estimated using the following explanation. In order to go from one minimum to another in the configuration space, it is necessary to overcome a saddle point with energy E_{h0}. The stresses necessary for it are close to the theoretical strength. Therefore, setting $\sigma_t \approx \sigma_c$, we find from (3) for InAs that $E_{h0} \approx 10^{-3}$ eV/atom. It is obvious that $E_h < E_{h0}$.

Analysis of the expression (2) shows that the probability of formation of highly-excited states increases with growing σ. Structurally, these states can be considered as a cluster with short-range order of atoms different from the initial state. The process of their formation depends on the size of stress concentrator through the number of atoms in its vicinity, on the properties of crystal and value of excitation energy E_h. With the changing structural state of a specimen as a result of machining, σ changes locally in the vicinity of a stress concentrator, and the probability of formation of highly-excited states increases. The square-law dependence of E on σ results in a strong dependence of η on x. The dependence on E_h is weaker, it is root-law. Therefore, the condition $\sigma < \sigma_t < \sigma_c$ (σ_c is the theoretical strength) results in the opportunity for defects nucleation at the stresses lower by one-two orders of magnitude than the theoretical strength. However, the probability of their nucleation at $x < 0.1$ is very small and the crystal behaves as an elastic body.

Further evolution of the formed highly-excited state is determined by the character of stress distribution in the active zone of stress concentrator. Stress relief can result in irreversible changes in crystal such as the formation of defects. Criterion of the formation of defects is the following:

$$E_{hc} > E_d. \qquad (4)$$

If this condition is not satisfied, structures with short-range order not characteristic of the crystal are conserved in it.

Thus, under such consideration, breaking through a high potential barrier is not required for the nucleation of a defect. Having determined experimentally the nonequilibrium number of defects formed in a crystal as a result of machining (change of the parameter of deviation from stoichiometry), we can estimate the energies of their formation.

3. EXPERIMENTAL TECHNIQUE

The processes of the formation of point defects, their diffusion in the fields of elastic stresses, and changes of stoichiometry, were studied using X-ray diffractometry methods [7, 8]. The integrated intensities I_R of the allowed 400 and quasi-forbidden 200 reflections were measured with the use of CuK_α irradiation. The technique described in [8] is sensitive to changes of stoichiometry of crystals. The essence of the technique is that $I_R \sim (c_\alpha f_\alpha - c_\beta f_\beta)$ (c_i is the atomic concentration of components, f_i is the function of atomic dissipation of components) and the slightest changes in the concentration of components at the level ~ 10^{17} cm^{-3} result in variations of integrated intensity, which are recorded experimentally. As is shown in [7, 8], the intensity of these reflections is low-sensitive to the macrodeformations of a crystal, because the ratio of reflecting capacities calculated for perfect-mosaic and perfect crystals equals ~ 1. The macroscopic bend of crystals was examined according to changing position of the reflection peak (400 reflection) in the course of crystal scanning by X-ray beam. The microscopic bend was measured from the change of angular distance between the lines of CuK_α doublet.

The (100) InAs single-crystalline plates 150–400 μm in thickness doped with S and Sn and having density of dislocations of the order of magnitude 10^4 cm^{-2} were studied. Upon measuring the parameters in the initial state, the back surfaces of the plates were ground using M20 abrasive, and the measurements were carried out again in the same areas at certain time intervals *t*.

4. RESULTS AND DISCUSSION

The basic experimental results are presented in Fig. 1. It can be seen that the crystals in the initial state have a surplus of metal component (the value 1.00 on the ordinate in the Figure corresponds to the level of stoichiometric composition). The integrated intensity decreases drastically after grinding down to the level below the stoichiometric value, *i.e.*, As atoms predominate, and the crystal is bent with the camber on the disturbed side. The bend value is affected by the depth

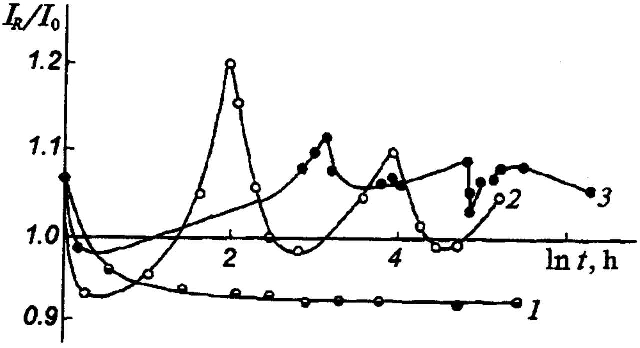

Figure 1. Time variations of the ratio between the integrated intensities of X-ray 200 reflections of the machined crystal, I_R, and the value I_0 of the stoichiometric crystal (degree of changing nonstoichiometry). *1*—initial elastic-deformed crystal, *2*, *3*—machined (ground) crystals 170 and 400 μm in thickness, respectively.

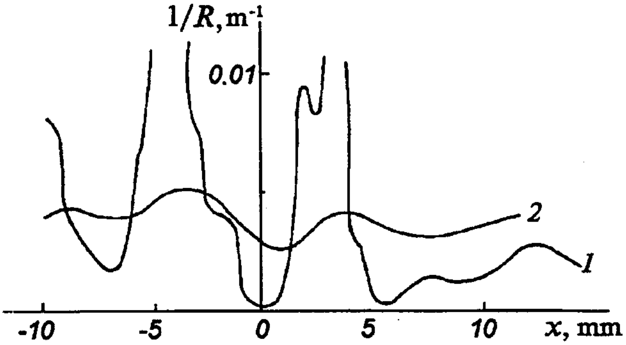

Figure 2. Changes of the curvature parameter of InAs plate ($t = 170$ μm) along [100] direction. *1*, *2*—crystals with the disturbed layer 53 and 7 μm in thickness, respectively.

of disturbed layer and plate thickness. It follows from the experiment that the decrease of intensity appears to be different depending on the bend radius of a plate. The average curvature of a plate appears to be highly modulated (Fig. 2), and it oscillates with the step of some hundred nanometers. This testifies that the deformation in the studied disturbed crystal layer is laterally inhomogeneous despite the spatial remoteness of the disturbed layer. Therefore the effect of decreasing intensity as a result of grinding is variously displayed in various regions of the plate. It emphasizes once again the importance of taking account the distribution of deformation along the surface of plates in the study of point defects behaviour. Besides, the modulation of curvature is concerned with macroscopic inhomogeneities of the distribution over the plate area of the components (impurities), which are the stress concentrators.

It follows from [9] that these modulations of curvature give rise to the lateral component of deformation (along the surface of a plate) and consequently to the distribution gradient of intrinsic point defects and impurities. This component under normal (equilibrium) conditions does not manifest itself, and this deformation mechanism is initiated only in the case of disturbed system equilibrium (grinding of the back side).

Thus, decrease of integrated intensity immediately after grinding can be explained also by the effect of this component. The level of local stresses after grinding reaches the critical size, and the equalization (redistribution) of the components concentration begins in the plane of a plate.

In turn, the disturbed layer is a powerful source of point and extended defects. As is shown in [10], the disturbed layer creates point defects not only in this layer and in its vicinity, but also in the whole volume of the crystal. The mechanism of such defects formation is described above. In the field of elastic strains, the diffusion movement of point defects to the working surface begins. Since point defects are available in the whole volume, this movement has to be initiated immediately after machining and reaches a maximum at the instant the point defects from the disturbed layer attain the working surface of the plate by the way of diffusion. Thus, the first maximum is formed in the dependence $I_R = f(t)$ (Fig. 1). At the instant the defects attain the working surface, the deformation level at local inhomogeneities reaches again the critical size and strain relief takes place to account for the lateral component of the diffusion of intrinsic point defects and impurities.

Inasmuch as the InAs crystal is a complex compound, defects of various types with different diffusion rates are available in it, *i.e.*, the defects reach the working surface in different times. Thus, it is possible to explain the presence of several maxima in the experimental dependence of relaxation in the point defects system.

Analyse now the energy aspects of point defects formation in the course of machining. In view of (1)–(3), the equation (4) can be written as

$$E_d < n l^3 E_h \eta, \tag{5}$$

where l is the characteristic size of stress concentrator (it is determined in our case by the depth of disturbed layer).

The parameter η has the meaning of the relative concentration of highly-excited atoms, N_h, which is estimated from the variation of integrated intensity of the reflection 200 ($\Delta I \sim N_h$), and its value is equal to $\sim 10^{18}$–10^{19} cm^{-3}. Having calculated σ from the radius of curvature of a plate similar to [12] and using the formula (3), we obtain the estimated value E_h. The parameters for E_d calculation are presented in the Table. Substituting the obtained values in (5), we find that E_d changes in the range ~ 0.1–0.5 eV.

These are the defects which carry out the mass transfer from the zone of stress concentrator in the field of elastic strains to the working

TABLE. Parameters for the calculation of the activation energy of point defects.

N_h, cm^{-3}	η	x	σ_t, dyne/cm^2	E_h, eV	E_d, eV
10^{18}	10^{-4}	0.33	$1.20 \cdot 10^9$	$5 \cdot 10^{-5}$	0.1
10^{19}	10^{-3}	0.38	$1.05 \cdot 10^9$	$4 \cdot 10^{-5}$	0.5

$n = 1.8 \cdot 10^{22}$ cm^{-3}, $l \approx 10^{-5}$ cm, $\sigma_{\exp} = 4.04 \cdot 10^8$ dyne/cm^2, $\sigma_c \approx 2.8 \cdot 10^{10}$ dyne/cm^2.

surface of a plate. This statement is supported by the fact that the oscillations are not observed experimentally in the case of the crystal deformed without disturbed layer, though the level of intrinsic point defects in the crystal equals ~ $10^{17}-10^{18}$ cm^{-3}. If the band of highly-excited states has several levels, than several types of defects can be originated simultaneously in the crystal, which is consecutively recorded in the experimental dependence.

As mentioned above, the movement of intrinsic point defects and impurities is of purely diffusion nature. Hence, the diffusion coefficients of one or other crystal defect in the field of elastic strains can be estimated. The analysis of experimental results points to the change of diffusion coefficient by orders of magnitude in the direction of increasing value. Such considerable change is indicative of the large contribution of the elastic strains caused by the presence of a disturbed layer to the diffusion processes in the volume of a crystal. This result can be explained taking into account the elastic properties of InAs (high brittleness and low strength). Furthermore, as is known from [11], the disturbed layer gives rise to the formation of a region with large density of dislocations, which being the drains (sources) of point defects can considerably change the diffusion conditions.

5. CONCLUSION

As the preliminary studies show, the period of integrated intensity oscillations depends on the thickness of crystal, type of machining, and degree of doping. After removal of the disturbed layer by means of chemical etching, the parameters of substrates do not return to the initial values.

Thus, machining of the back surface of plates, even in the case of considerable thickness (~ 400 μm), has a substantial effect on the processes of defect formation. The elastic stresses arising in the course of machining are the essential factor determining the effective diffusion coefficient and, hence, physical properties of the substrates. The changes taking place in crystal substrates during storage result in the degradation of parameters of devices.

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