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Vacancy clusters in plastically deformed semiconductors

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Abstract. Experimental investigations of plastically deformed elemental and III–V semiconductors prove that a high number of vacancies and vacancy clusters are formed. The formation of point defects by the motion of jogged dislocations is analysed. Vacancies formed behind the jog are not stable as a simple chain of vacancies. Instead, they are transformed immediately to stable three-dimensional agglomerates. The stability of various vacancy clusters has been investigated by means of density-functional calculations. The positron lifetime in such clusters was calculated and compared to experimental results. The association of open-volume defects with the dislocation can be derived from positron lifetime measurements. The analysis in a positron-trapping model characterizes the dislocation as a combined defect. The undisturbed dislocation line is a precursor trap for the positron capture in a deep trap related to the vacancies bound to the dislocation.

1. Introduction

The Alexander–Haasen model gives an empirical description of the lower yield stress [1]. The dislocation motion is characterized by the nucleation and migration of double kinks in the Peierls potential. The activation energy of the flow stress is identical to the activation energy of the glide velocity. The role of point defects is recognized in dislocation relaxation by climb at later stages of the stress–strain curve [2]. However, there is experimental evidence that point defects are already generated during plastic deformation at very low strains and/or rather low temperatures. The question of how the formation of intrinsic point defects can be reconciled with the elementary steps of dislocation glide remains open. A possible mechanism is the jog dragging, as proposed by Mott [3]. A first quantitative elaboration was given by Barrett and Nix [4]. The main source of jogs is the cutting of dislocations belonging to different slip systems or the cross slip of screw dislocations. The structure of a possible dissociated jog configuration on a screw dislocation in the fcc lattice is shown in figure 1. In the jog plane, a Shockley and a Frank partial dislocation are formed. The latter one can only follow the glide motion of the screw dislocation by emission or absorption of point defects. The shift of the jog by a perfect Burgers vector requires in the diamond structure due to the diatomic basis the emission or absorption of two atoms. These atoms are of a different type in the sphalerite structure. For example, in GaAs, there are four possible elementary steps for the growth of the extra half-plane: (i) V_{Ga} emission and V_{As} emission; (ii) V_{Ga} emission and As_i absorption; (iii) Ga_i absorption and V_{As} emission; (iv) Ga_i absorption and As_i absorption [5]. The cut-back

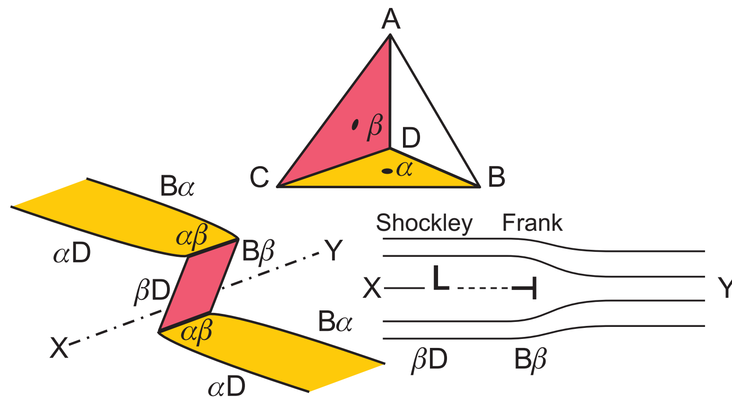

Figure 1. The structure of an extended jog in the acute-angle configuration on a screw dislocation with the Burgers vector DB. The Thompson tetrahedron is shown to indicate the corresponding slip planes and Burgers vectors. The X–Y cut illustrates the dissociation of the jog in a Shockley and a Frank partial (Burgers vectors βD and Bβ). The latter one has a pure edge character and can only follow the glide motion of the screw by emission or absorption of point defects.

of the extra half-plane of the jog is connected with the opposite processes. A very beautiful demonstration of the emission of vacancies by a jogged dislocation in copper has been given recently by means of large-scale molecular dynamics simulations by Zhou *et al* [6]. Vacancies have been formed behind the jog as monovacancies or in the form of short rows.

The question of the types of the point defects emitted and possible secondary reactions from the cases (i) to (iv) was the starting point of our own investigations. We would like to know whether longer chains of vacancies emitted by jog dragging can be observed, as predicted by Tarbaev *et al* [7]. We used positron annihilation as a sensitive tool to detect vacancy-type defects generated by plastic deformation [8].

2. Experiments and theoretical calculations

Deformation experiments were carried out under uniaxial compression of $4 \times 4 \times 12$ mm^3 bars in [001], [110], and [213] directions with constant strain rates between 9×10^{-6} and 6×10^{-3} s^{-1}. The deformation temperatures of doped and undoped Si and GaAs crystals were in the range 600 to 1100 K. The maximum strain was 1 to 27%. Conventional positron lifetime measurements were performed using a fast–fast spectrometer. A ^{22}NaCl source was deposited on a thin Al foil and placed in a sandwich composed of identically treated samples. A closed-cycle He cryostat was used for measurements between 15 and 600 K. 1.5×10^6 to 6×10^6 events were collected for a complete positron lifetime spectrum.

Due to the presence of various types of defect, the analysis of positron trapping in deformed semiconductors is rather complicated. The dislocations themselves are regarded as combined traps [9]. The regular dislocation line represents a shallow positron trap with a low binding energy for positrons. A thermally induced re-escape of the positron is highly possible at elevated temperatures T. Certain types of defect in the dislocation core, e.g. bound vacancies, may act as deep states. The positron is transferred from the shallow level to the deep bound state with a high transition rate. In addition to the dislocations, other positron traps must be taken into account in the trapping model. Vacancies and vacancy clusters are deep traps; negatively charged antisite defects act as shallow positron traps. The solution of the rate equations of positron trapping and annihilation in deformation-induced point defects and dislocations

gives the positron lifetime spectrum, which is the time derivative of the decay spectrum, $|\dot{n}(t)| = \sum_{i=1}^{N+1} I_i \lambda_i \exp(-\lambda_i t)$. N is the number of different defect types, I_i the intensity of the ith component with the annihilation rate λ_i, t the time. The defect-specific positron lifetime $\tau_i = \tau_{dj}$ is the reciprocal of the corresponding annihilation rate ($i > 1$, $j = i - 1$ is the counting index of defects). A simplified scheme including a dislocation and a vacancy-type defect can be analytically solved and gives a four-component lifetime spectrum [10]. However, a reliable decomposition of experimental positron lifetime spectra into four components is not possible without further assumptions. In such a case, only the average positron lifetime, $\bar{\tau} = \sum_{i=1}^{N+1} I_i \tau_i$, can be used. The measurement of $\bar{\tau}$ as a function of the sample temperature and after thermal treatment of the sample can provide information on the defect types present.

In order to investigate the stability of vacancy chains or other vacancy agglomerates, calculations with a self-consistent charge density-functional-based tight-binding (SCC-DFTB) method were made. The outline of the simulation scheme was given by Elstner *et al* [11]. This methods allowed the use of very large supercells with 512 atoms, which are needed to avoid defect–defect interactions for vacancy clusters. We used only charge-neutral supercells, i.e. GaAs supercells with equal numbers of missing gallium and arsenic atoms. Due to the electron-counting rule, this should lead for GaAs to neutral configurations over a wide range of the Fermi level. The defect formation energies are independent of the chemical potential and have an absolute value. This allows the direct comparison of the formation energies of various vacancy agglomerates.

The positron lifetimes were calculated using the superimposed-atom model [12]. The unrelaxed atomic positions as well as the positions determined by the SCC-DFTB method were taken for the calculation. The theoretical data were scaled to the experimental bulk lifetime.

3. Results and discussion

Above room temperature, the capture of positrons in deformation-induced shallow traps can be neglected, and a three-component decomposition is possible. In addition to the reduced bulk lifetime, two defect-related lifetimes are obtained: $\tau_{d1} = 260 \pm 5$ ps and $\tau_{d2} = 477 \pm 20$ ps for GaAs deformed at 673 K at a strain rate of 1.6×10^{-5} s^{-1} and $\tau_{d1} = 285 \pm 20$ ps and $\tau_{d2} = 485 \pm 30$ ps for Si deformed at 1073 K at a strain rate of 1.2×10^{-5} s^{-1}. Higher strain rates lead to significantly higher values of τ_{d2}: 509 ± 5 ps (GaAs) and 600 ± 50 ps (Si).

The d1 components indicate the presence of a defect having an open volume of a monovacancy. The thermal stability of this defect was investigated in annealing experiments. They are much more stable compared to monovacancies found after low-temperature electron irradiation. The annealing of the d1 defects starts in GaAs at 850 K, in Si at 950 K. The annealing stage is very broad and can hardly be related to a single activation energy. There is a correlation with the dislocation density: in samples with very few dislocations, the d1 component is missing. On the other hand, this lifetime component can be completely annealed. In GaAs annealed at 1000 K, dislocations are still present, but the d1 components have vanished [13]. It is concluded that d1 is related to vacancies bound to dislocations.

The result of a positron lifetime measurement on deformed GaAs is shown in figure 2. Due to positron trapping in shallow traps having an annihilation rate close to the bulk value, the average lifetime decreases in the low-temperature region. No three-component decomposition is possible below 110 K: there is complete trapping in defects. Above that temperature, the three lifetimes τ_1, $\tau_2 = \tau_{d1}$, and $\tau_3 = \tau_{d2}$ are obtained from the decomposition. The reduced positron bulk lifetime τ_1 is not related to defects and is not shown in figure 2. The trapping rates of the defects d1 and d2, κ_{d1} and κ_{d2}, can be calculated for sample temperatures >110 K. They

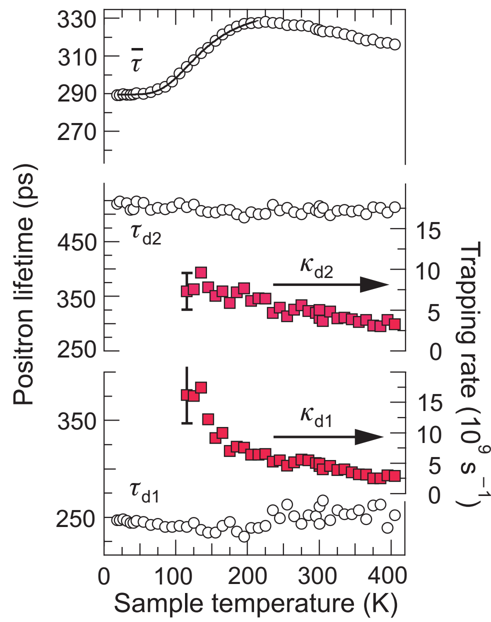

Figure 2. Positron lifetime measurement for plastically deformed GaAs. The upper panel shows the average positron lifetime $\bar{\tau}$ as a function of the sample temperature. In the lower part, the result of the decomposition is given. The defect-related lifetimes τ_{d1}, τ_{d2} and the positron trapping rates κ_{d1}, κ_{d2} are shown. Complete positron trapping in defects occurs below 110 K, and no trapping rate can be determined. The sample was deformed at 1073 K in the [110] direction with a strain rate of 4.8×10^{-5} s^{-1} up to a strain of 10%.

are related to the densities of the defects d1 and d2. The variation of κ_{dj} with the temperature due to the charge state of the defects and the influence of shallow positron traps is discussed elsewhere [14].

The longer-lifetime component d2 is much larger than that of monovacancies or nearest-neighbour divacancies. In order to identify the size of the vacancy clusters, the results of the SCC-DFTB calculations were used to calculate the defect-specific positron lifetime. We examined different three-dimensional vacancy clusters in Si and GaAs in order to determine their stability. There are a huge number of possible configurations. We used a straightforward construction scheme, assuming that only closed structures have a minimum energy [15]. The first step was the formation of hexagonal ring-like structures. The structures of V_6 and other closed configurations are shown in figure 3 for the case of GaAs. To compare the energies of the different clusters in Si (GaAs), the energy gain produced by adding a monovacancy (divacancy) to a stable cluster of $n-1$ ($n-2$) vacancies was calculated. This corresponds to the negative dissociation energy of V_n into V_{n-1} + V ($V_{n-2} + V_2$) for Si (GaAs). The result is plotted for GaAs in the upper panel of figure 4. The energy gain as a function of the cluster size was also calculated for Si [16]. The smallest stable structure, with respect to dissociation, is found to be V_{12} in GaAs, whereas it is V_6 in Si. The result for Si is in accordance with earlier results based on simple bond-counting rules [17].

No calculations on the stability of vacancy agglomerates in compound semiconductors are known from the literature. The special stability of V_{12} in GaAs can be understood from the relaxation of the structure. The dominant feature is the formation of an As–As dimer and a Ga–Ga dimer bond [15]. This reduces the number of dangling bonds and thus lowers the total

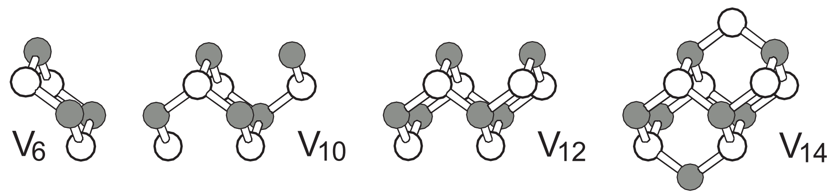

Figure 3. Structure of the unrelaxed vacancy clusters V_6, V_{10}, V_{12}, and V_{14} in GaAs. White balls represent arsenic vacancies, dark balls gallium vacancies.

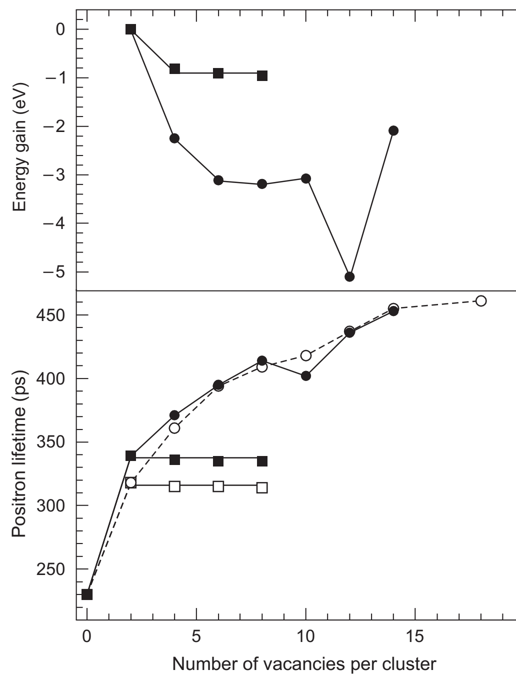

Figure 4. Energy gained by adding in GaAs a nearest-neighbour divacancy to an aggregate of $n-2$ vacancies. ■: vacancy chains in the ⟨112⟩ direction; ●: vacancy clusters. The lower panel shows the calculated positron lifetimes for the relaxed chains (■) and clusters (●), as well as the values for the unrelaxed structures (□, ○).

energy. A general feature of the relaxed vacancy structures in GaAs is the sp^2 hybridization of threefold-coordinated Ga atoms by emptying all dangling bonds. In contrast, all threefold As atoms exhibit a p^3 hybridization by filling the dangling bonds. The change in the hybridization leads to a further reduction of the total energy. The formation of dimers is already possible for V_{10}. However, some Ga atoms are not able to form energetically favourable threefold-coordinated sp^2 structures. Therefore, V_{10} is less stable than V_{12}.

Our calculations showed that the formation energy for chains of vacancies is much higher than that of vacancy clusters. There is no energy gain produced by elongation of the vacancy chain. Hence, if the vacancies are able to move along the chain, the initial configuration will be rearranged to a three-dimensional cluster with lower energy. This may happen without a diffusion step already at rather low temperatures.

The function of the energy gain versus the number of vacancies per cluster was also calculated for Si [16]. The next stable agglomerates after V_6 are V_{10} and V_{14}. These structures

are built up from adjacent hexagonal rings of vacancies and have minimum numbers of dangling bonds in the relaxed configuration. All atoms surrounding V_6 are fourfold coordinated, while in the V_{10} adamantine cage four atoms remain threefold coordinated. V_{14} has eight threefold-coordinated atoms. The increase in energy caused by the threefold-coordinated atoms is compensated by new bonds being formed close to the ideal bond length.

The result of the calculation of the positron lifetime is shown for GaAs in the lower panel of figure 4. The positron lifetime in vacancy chains stays on the same level, independently of the size. The defect-related lifetime is that of the divacancy, $\tau_{V_2} = 340$ ps (relaxed configuration). Such a lifetime component has not been observed in plastically deformed semiconductors. Together with the considerations about the stability of vacancy chains based on the total-energy calculations, the conclusion can be made that vacancy chains are not formed as a result of jog movement.

The positron lifetime in relaxed three-dimensional vacancy clusters increases monotonically with the number of vacancies per cluster. It tends to saturate above 450 ps. The especially stable V_{12} in GaAs exhibits a positron lifetime of 440 ps. It may be a good candidate for having the longer lifetime τ_{d2} observed in plastically deformed GaAs, if the large statistical error of that component and uncertainties of the calculation are taken into account. For Si, the positron lifetimes for the most stable agglomerates V_6, V_{10}, and V_{14} were calculated to be 375, 420, and 435 ps. The experimentally observed lifetime component d2 can therefore be attributed to V_{14}. The high value of 600 ps (509 ps) found for Si (GaAs) deformed at high strain rates cannot be attributed to a certain size of a vacancy cluster. Rather, it indicates positron trapping at the inner surface of larger agglomerates.

A similar result to that for GaAs was obtained for vacancy chains in Si. Independently of their size, the calculated positron lifetime is that of a divacancy, i.e. 300 ps.

The experimentally observed average lifetime decreases at low sample temperatures due to shallow positron traps (figure 2). In plastically deformed GaAs, such shallow traps are not the only regular dislocations; Ga_{As}^- antisites also appear. A fit of $\bar{\tau}$ as a function of the temperature can be made with the trapping model taking into account the positron capture in two deep traps and a shallow trap. The thermally induced detrapping from shallow traps can be described by

$$\frac{\delta}{\kappa} = \frac{m_+ k_B T}{2N_d \hbar} \operatorname{erf}^{-1}\left(-\frac{E_b}{k_B T}\right) \exp\left(-\frac{E_b}{k_B T}\right) \tag{1}$$

in the case of dislocations and

$$\frac{\delta}{\kappa} = \frac{1}{\rho}\left(\frac{m_+ k_B T}{2\pi\hbar}\right)^{3/2} \exp\left(-\frac{E_b}{k_B T}\right) \tag{2}$$

for point-like shallow traps. The differences between equations (1) and (2) are due to differences in the geometry and the character of the shallow traps [18]. κ is the trapping rate, δ the detrapping rate, m_+ the effective mass of the positron, and k_B the Boltzmann constant. The defect is characterized by the binding energy of the positron, E_b, and the density, N_d or ρ. These quantities are the fitting parameters.

A positron binding energy of 40 ± 3 meV is obtained from the fit for deformed GaAs. A similar value has been reported for Ga_{As}^- antisite defects generated by electron irradiation [19]. After annealing at 1030 K, shallow positron traps are still present. The energy E_b is now obtained from the fit as 27 ± 8 meV. This value does not change substantially, when equation (1) is applied instead of equation (2). The energy of binding of positrons to regular dislocations in Si has been obtained to be about 10 meV [20]. In conclusion, the smaller binding energy in GaAs found after annealing of the Ga_{As}^- antisites and other point defects may also be related to regular dislocation lines.

The formation of antisite defects during plastic deformation of GaAs can be understood as a result of jog dragging and the reaction of vacancies and interstitials emitted by the reactions (ii) and (iv) mentioned in section 1: $Ga_i + V_{As} \rightarrow Ga_{As}$ and $As_i + V_{Ga} \rightarrow As_{Ga}$. Evidence for the former antisite is not only found by means of positron annihilation, but also by means of electron paramagnetic resonance (EPR). The latter antisite defect was detected in plastically deformed GaAs by infrared absorption [21] and EPR measurements [5].

The intersection of dislocations leads to the formation of jogs or kinks depending on the Burgers vectors, the glide directions, and the line vectors. The resulting jog may not be glissile and its movement may result in the formation of point defects. The number of point defects per unit path length generated by the intersection of two dislocations and the subsequent climb of the jog can be calculated [22] as

$$N = \frac{1}{\Omega} \frac{\boldsymbol{\xi}_1 \cdot \boldsymbol{u} \times \boldsymbol{\xi}_2}{|\boldsymbol{\xi}_1 \cdot \boldsymbol{u} \times \boldsymbol{\xi}_2|} \boldsymbol{b}_1 \cdot \boldsymbol{u} \times \boldsymbol{b}_2.$$

Ω is the atomic volume and $\boldsymbol{u}$ the direction of the motion of the dislocation with the Burgers vector $\boldsymbol{b}_1$ and the line vector $\boldsymbol{\xi}_1$. $\boldsymbol{b}_2$ and $\boldsymbol{\xi}_2$ are the Burgers vector and the line vector of the second dislocation. The first term determines the sign, i.e. whether interstitials or vacancies are formed; the second one gives the number of point defects emitted. Jogs on edge dislocations can follow the glide motion and do not emit point defects.

Jogs can be easily shifted on the screw dislocation. As a result, superjogs with jump heights h higher than the magnitude of the Burgers vector can be formed. For h higher than a critical value, no point defects are directly emitted. Instead, dislocation dipoles are formed (figure 5).

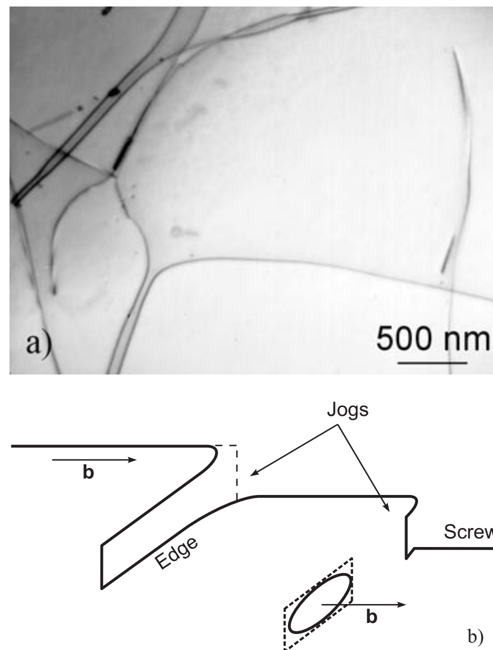

Figure 5. (a) A transmission electron microscopy image of plastically deformed GaAs showing the formation of dislocation dipoles. The sample was deformed at 825 K in the [110] direction at a strain rate of 1×10^{-4} s^{-1} up to 3% strain. (b) Elongation of edge dipoles at jogs on a screw dislocation. Prismatic loops may be formed as a result of the partial annihilation of the edge dislocations. For elementary jog heights, vacancies or interstitials are formed according to the sign of the jog.

The partial annihilation of the dipole may result in the formation of prismatic dislocation loops and point defects.

In conclusion, the formation of point defects during plastic deformation of semiconductors can be related to the dislocation motion. A basic mechanism is the emission or absorption of vacancies and interstitials by screw dislocations containing jogs. The formation of long rows of vacancies is energetically unfavourable. Stable three-dimensional vacancy agglomerates are formed in a primary process by atomic rearrangement directly at the climbing jog.

Acknowledgments

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