Direct Antisite Formation in Electron Irradiation of GaAs

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We investigate the antisite formation in GaAs by molecular dynamics simulation with a realistic many-atom potential. The recoil energies are chosen to correspond to the values encountered in electron irradiation experiments. The probability of forming antisites directly during the cascade is substantial. The antisite defects are stable and are likely to survive during long-term annealing. We estimate the angle-dependent threshold for antisite formation and discuss the creation mechanism. The cross sections for antisite and vacancy formation are compared.

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The antisite defects in III-V-type compound semiconductors have wide technological interest because of their electrical properties. For instance, As_{Ga} is related to the *EL*2 defect which is responsible for the semi-insulating behavior of GaAs [1,2]. Electron irradiation is commonly used to produce point defects in semiconductors due to the favorable range of recoil energy. When a nucleus is hit by an electron with kinetic energy in the MeV region, the transferred energy is a few tens of eV, which leads to the creation of a very limited amount of point defects in a single collision event. Formation of antisite defects in electron-irradiated III-V compound semiconductors has been intensively studied experimentally during the last decade, but the creation mechanism for antisites has remained a question of controversy.

The early studies proposed that antisites are created when mobile interstitials produced in the irradiation replace substitutional impurities or attach to defect complexes [3,4]. The irradiations were performed at room temperature and did not reveal whether the antisites were created directly in the collision events or only by the proposed interactions of mobile defects. Recently irradiation experiments have been performed at lower temperatures, thus excluding the high temperature effects, e.g., interaction and migration of point defects. Corbel *et al.* [5] found a high number of negative ions identified as Ga_{As}. Krambrock *et al.* [6] reported the identification of the formation of As_{Ga}. Pillukat and Ehrhart [7] observed the creation of antisite related defect complexes. However, these results do not reveal the microscopic mechanism for direct antisite creation in electron irradiation. In this Letter we report simulations which clearly manifest that antisites are produced directly during the electron irradiation. We show that focused collisions lead to replacement cascades and that the created antisites are stable.

Molecular dynamics (MD) simulation is a powerful tool in modeling radiation-induced collision cascades in various materials [8]. For compound semiconductors the MD approach has recently become possible due to the development of semiempirical many-atom potentials which give a realistic description of covalently bonded systems. However, the maximum time scale available for these types of simulations is limited to a few nanoseconds with the present computer capacity. Thus the long-term migration and interaction of defects are difficult to effectively study with simulations. On the other hand, simulations can give an exact microscopic view of atomic collision events during electron irradiation. A near-equilibrium state after the primary atomic recoil is reached in a few picoseconds; this can be easily accomplished in MD simulations.

Here we report cascade simulations with the Tersoff potential [9], for which the parametrization for GaAs has been developed by Smith [10]. Sayed *et al.* [11] have improved the Smith parametrization by refitting the parameters for As-Ga interactions, thus correcting the too weak angle-dependent term. We have performed simulations with both parametrizations, and the results do not depend qualitatively on the parameter set, verifying the reliability of the model. All results presented below are from the simulations made with the improved parametrization. However, we see some quantitative changes in the amount of produced defects with the two models, which will be described below.

The initial configuration for each reported simulation was an ideal zinc-blende lattice at zero temperature. The electron irradiation was simulated by giving an impulse to an atom so that the recoil energy ranged from 10 to 70 eV. In head-on collisions between relativistic electrons and Ga or As atoms this would correspond approximately to 0.25 to 1.2 MeV in electron kinetic energy. In this recoil energy range no high-energy modifications to the repulsive potential are necessary.

The simulations were performed with two system sizes. The smaller (larger) one consisted of 1728 (4096) atoms, which corresponds to 6 (8) atomic unit cells in each Cartesian direction. The simulations with recoil energies up to 40 eV were carried out in the smaller ensemble. With larger energies we saw clear finite size effects with the smaller system and therefore the system size was increased to 8 unit cells per side when recoil energies over 40 eV were investigated. The knock-on direction

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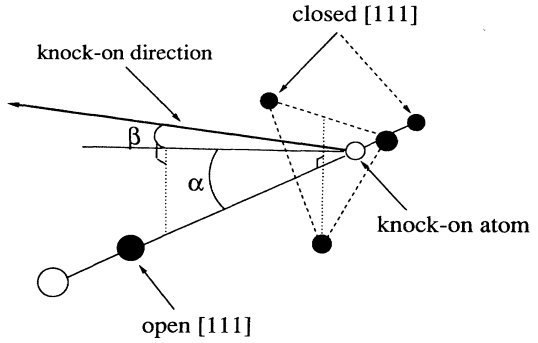

FIG. 1. The recoil geometry and the angles, α and β, which specify the knock-on direction.

was varied so that the full crystal symmetry was covered. Each chosen direction was labeled by two angles α and β, which are illustrated in Fig. 1.

Both angles were varied between 0 and 54.7 deg (this corresponds to half the bond angle) so that the range was scanned with 20 steps, i.e., about 2.74 deg per step. The discretization of the β axis was modified by a sinusoidal term in order to keep the solid angle for every direction constant ($d\Omega = d\alpha \sin\beta d\beta$). Thus, the solid angle covering the crystal symmetry was scanned with 441 directions, each corresponding to a full MD simulation. The open and closed [111] directions correspond to the cases when an atom is recoiled away from its nearest neighbor in the [111] direction or toward it.

The initial site of the primary knock-on atom (PKA) in the simulation cell was chosen for each direction to maximize the free volume available to the collision cascade before reaching the boundaries. The simulations were performed symmetrically with both Ga and As as the PKA. A variable time step integration routine was used which allowed the fastest atom to move 0.02 Å during one step. The kinetic energy dissipation at the boundaries was described by Langevin scaling of the velocities of the two outermost atomic layers at regular intervals to zero. This prevents the reflection of the kinetic energy pulse from the boundaries. The damping boundary absorbs also the inserted momentum which otherwise would cause net motion of the entire system. The prevention of the reflection of the kinetic energy pulse from the boundaries was found to be an essential prerequisite for consistency of the results. The same observation has been made by Sayed *et al.* when investigating the atomic displacements with a similar technique [11].

The structural changes caused by the recoiling atom were monitored by counting the number of produced vacancies and antisites. A nonoccupied lattice site was labeled a vacancy if the distance to the closest lattice atom was over 1.0 Å, which is roughly 0.4 times the equilibrium bond length in GaAs (2.45 Å). Correspondingly, if we could detect an As atom within 1.0 Å from an empty Ga site this was labeled an As antisite (As_{Ga}) and naturally vice versa for Ga_{As}. The defect analysis was done at 2.0 and 2.5 ps after the knock-on. After the second analysis a single run was terminated and the next simulation was started with a different knock-on direction. The consistency in the results of the two analysis instants indicated no rapid structural evolution, and therefore all the results shown here are at 2.5 ps. In Fig. 2 the directional

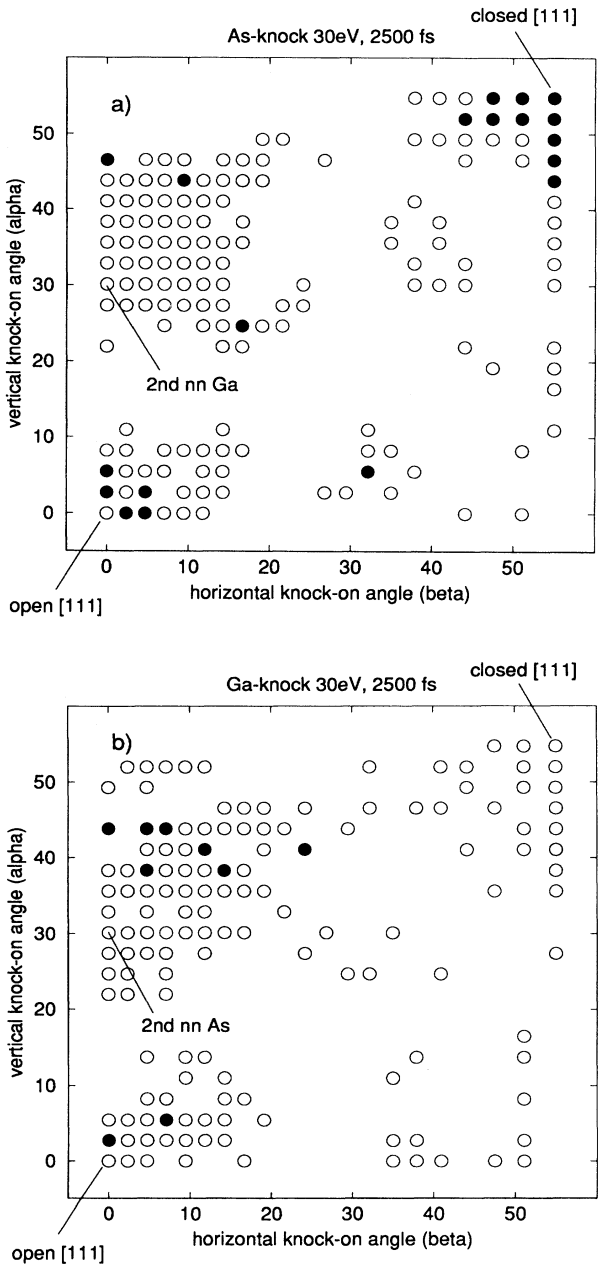

FIG. 2. The anisotropy of antisite creation with 30 eV recoil energy (a) As and (b) Ga as the PKA. An open circle denotes the creation of one antisite of either type and a filled one the creation of two antisites.

analysis of antisite creation with 30 eV recoil energy is presented. A marker in the plot denotes that at least one antisite has been created for that recoil direction.

The pattern for antisite formation is qualitatively similar when As [Fig. 2(a)] or Ga [Fig. 2(b)] has been given the initial impulse. The immediate observation in both cases is that the antisite formation is concentrated to some specific directions of which the most remarkable are the open and closed [111] directions. Another clearly noticed direction favoring antisite creation is from the PKA toward the second nearest neighbor of the opposite type. The principal mechanism for antisite creation was observed to be a collision sequence where the PKA displaces an atom of the opposite type from its equilibrium site and occupies the released site. We observed focusing cascades in the open and closed [111] directions where the replacement mechanism occurs several times in a billiard ball fashion creating a "chain" of antisites. In Fig. 3 the atomic positions in the [111] plane are illustrated after a collision cascade which was initiated by a 70 eV As recoil to the open [111] direction. The creation of a sequence of antisites is clearly seen. In addition, there exists a vacancy at the PKA initial site and one interstitial is created at the end of the collision sequence when the kinetic energy of the last displaced atom does not exceed the threshold for further replacements. In this specific case the last displaced atom is Ga, which found its interstitial position close to the last created As_{Ga}. Scanning over a wide recoil energy range revealed no considerable anisotropy with respect to the open and closed [111] directions or to the PKA type. In positron experiments [5,12] "isolated" Ga_{As} well separated from V_{Ga} have been observed. The existence of focused cascades explains that an antisite can be formed far from the vacant site of the PKA.

The average probability to produce an antisite as a function of knock-on energy is presented in Fig. 4. Each probability has been calculated by counting the number of antisites produced with a specific recoil energy and dividing the amount by the number of angular scan points (441). The two curves for As (Ga) as the PKA describe the formation of As_{Ga} (Ga_{As}) and Ga_{As} (As_{Ga}). The threshold energy for the antisite creation is approximately 15 eV for using either type as the recoil atom. The probability for the antisite creation increases roughly linearly as a function of energy and no considerable asymmetry with respect to the sublattice species can be observed. Direct comparison between antisite production rates given by the present simulations and experiments [3,4,12] is not straightforward. For that purpose we would need the momentum transfer cross section for the relativistic electrons moving through the GaAs lattice. If we make a rough estimate for this by using the formula by Mott [13] for free atoms, the production rates are of the same order of magnitude in our simulations and experiments [4,12].

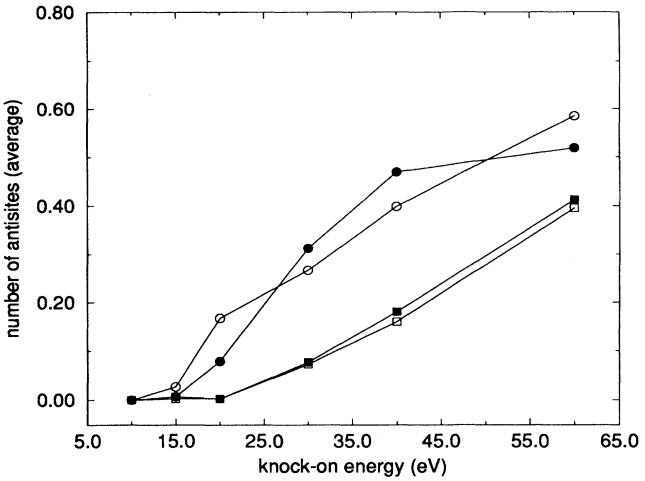

FIG. 4. The average number of antisites as a function of knock-on energy. Filled (open) markers denote As (Ga) as the PKA, circles As (Ga_{As}) and squares Ga_{As} (As_{Ga}).

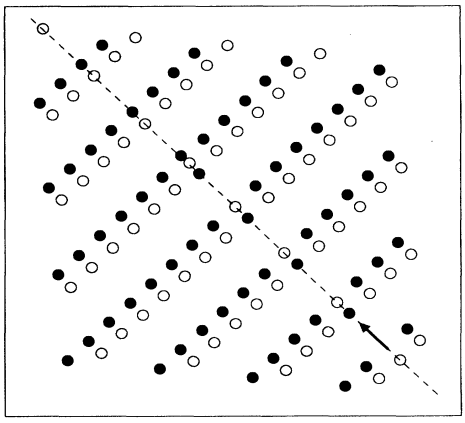

FIG. 3. Positions of the atoms in the [111] plane 2.5 ps after a 70 eV As recoil to the open [111] direction. The Ga interstitial is situated 0.8 Å away from the [111] plane.

The observed formation of vacancies is not isotropic but shows pronounced directional dependence as in the case of antisites. The average number of produced vacancies increases almost linearly as a function of the knock-on energy, following the prediction of the Kinchin-Pease model [14]. The threshold energy for vacancy formation is slightly less than 10 eV in agreement with the work by Sayed *et al.* [11]. The probability for vacancy formation is approximately a magnitude greater than for antisites. Experimentally it is well verified that the recombination of vacancies and interstitials occurs at much lower temperatures than those where the antisites are destroyed [15]. This means that although considerably more vacancies and interstitials than antisites are produced at low temperatures according to our present study, the relative amount of these types of defects observed at room temperature can experience large changes due to the recombi-

nation vacancies and interstitials and the persistence of antisites. This explains the differences between the present study and the experimental results where the estimated vacancy and antisite concentrations are of the same order of magnitude after annealing at room temperature [12].

With the original parametrization by Smith the threshold for antisite creation is roughly 20 eV, and the average production probabilities decrease by a factor of 2. However, the same directions were seen to favor antisite creation with focused cascades. The original Smith parametrization produces roughly twice as many vacancies as the improved parametrization, in accordance with the decrease in the amount of antisites. We therefore conclude that the shift in the number of produced defects can be explained by the change in the stiffness of bond-angle term; the too weak angular term in the original parametrization is incapable of reestablishing the tetrahedral coordination broken during the collision cascade.

The small difference in the atomic weights of As and Ga leads to an almost complete momentum transfer between the atoms in head-on collisions. This is clearly manifested by the creation of a sequence of antisites in the [111] direction. However, in other compound semiconductor materials, such as AlAs or InP, the ratio between the masses of the atoms deviates considerably from unity. This leads to an incomplete momentum transfer between the colliding atoms and is expected to change the collision cascades. We investigated the mass effect by performing simulations first with the parametrization by GaAs but reducing the mass of Ga artificially to half of its original value. Using the parametrization for AlAs [11] enabled the study of the mass effect with a more realistic model. We scanned with both models the open and closed [111] directions with 5 eV steps from 15 to 70 eV and used both sublattice species as the PKA. The results indicate that the amount of produced antisites is considerably reduced compared with the "real" GaAs. The sequences of antisites observed in GaAs could not be reproduced.

Experimentally it has been observed that the irradiation-induced As antisites have different properties compared with the native ones. In particular, the metastable state associated with the native As antisite could not be well detected in some experiments with electron-irradiated GaAs [7,16]. A recent positron lifetime study has shown the existence of the metastable state with modified properties [12]. The differences compared with the native defects have been related to the presence of other defects surrounding the antisites. We point out that our simulations support this explanation. This was shown above by the creation of defect complexes where antisites are not isolated but are related to other antisites, interstitials, and vacancies.

In conclusion, we have for the first time demonstrated with a realistic computer simulation that stable antisites are created directly during electron irradiation of GaAs. The results indicate that the creation of antisites is anisotropic near the formation threshold, which we estimate to be approximately 15 eV. The antisites are observed to be formed directly by a replacement mechanism, and no pronounced asymmetry in the relative amount of As_{Ga} and Ga_{As} type defects can be observed. The probability for vacancy production is considerably larger than for antisites. The focused cascades, typical in GaAs, resulting in a sequence of antisites are not likely to occur in compound semiconductors with large mass difference between the atoms in the two sublattices, e.g., AlAs.

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