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Doping-induced suppression of dislocation formation in semiconductors

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A mechanism explaining suppression of dislocation formation in doped semiconductors is proposed. The mechanism is based on the recently introduced concept of amphoteric native defects. It is shown that supersaturation of vacancylike defects depends on the Fermi energy and thus also on the doping level. The calculated dependence of supersaturation on the doping level quantitatively accounts for experimentally observed trends in dislocation suppression in GaAs and InP.

Understanding of the physical processes leading to the formation of dislocations in semiconductors is of great basic interest and of practical importance. In melt-grown, undoped compound semiconductors, the dislocation density ranges from 10^3 to 10^6 cm^{-2}.[1] It has been demonstrated that in some instances doping with electrically active (EA) or isoelectronic (IE) atoms results in a dramatic reduction of the dislocation density. At high enough doping levels dislocation-free crystals can be prepared.[1,2] Several attempts have been made to explain this phenomenon in terms of solute hardening, assuming either formation of native-defect–impurity complexes[3] or hardening induced by strain around isoelectronic impurities.[4] These proposals have met with only limited success and are in clear disagreement with recent high temperature measurements of the hardness of Si- and In-doped GaAs crystals.[5,6] These experiments clearly showed that although both of these dopants are very effective in reducing the dislocation density, they have no significant effect on the high-temperature critically resolved shear stress.

In this paper we propose a new mechanism of dislocation density reduction in doped semiconductors. The mechanism is based on the recently introduced concept of amphoteric native defects, i.e., defects whose identity and formation energy depend on the Fermi energy position. It has been shown previously that amphoteric native defects offer the basis for a simple, common understanding of a multiplicity of phenomena in semiconductors and at metal-semiconductor interfaces.[7,8] Here we show that the longstanding and controversial discussion as to which physical processes are leading to suppression of dislocation density in doped semiconductors can be quantitatively understood in terms of the same concept.

It has been recognized in the early studies of crystalline solids that one of the basic mechanisms of dislocation formation is condensation of native defects.[9,10] Condensation of vacancies[11,12] as well as interstitials[13,14] were invoked to explain some of the experimental observations on dislocation formations in semiconductors. A very distinct dependence of the dislocation density on the stoichiometry and the doping level observed in small-diameter GaAs crystals have led to a suggestion that the process of dislocation formation occurs via condensation of the vacancies.[11,12] However, no quantitative description of the process could be provided at that time.

The process of vacancy condensation begins in the initial stages of the post-growth cooling of the crystal.[10] In general, when the crystal temperature is lowered from $T+\Delta T$ to T the concentration of vacancies will exceed the equilibrium value at T. This supersaturation of vacancies will induce formation of vacancy complexes in the form of vacancy disks. The disks act as efficient vacancy sinks and, as has been discussed in Ref. 10 for high enough supersaturation, the disks collapse to form stacking faults surrounded by a dislocation ring. The condition for the dislocation formation is that supersaturation exceeds a critical value. The critical supersaturation corresponds to the situation when an increase in the strain energy of expanding dislocation ring is compensated by the decrease of the free energy of supersaturated vacancies. Therefore, understanding of dislocation formation in semiconductors requires quantitative knowledge of the factors affecting formation of vacancies. For vacancies with temperature-dependent concentration given by $C(T)=C_0\exp(-E_f/kT)$ the condition for the dislocation formation is that the energy[10]

$$kT\ln\frac{C(T+\Delta T)}{C(T)}=kT\ln\left[\frac{C(T)+dC/dT\Delta T}{C(T)}\right]\cong k\frac{TdC}{CdT}\Delta T \qquad (1)$$

exceeds the increase of the strain energy of a dislocation ring expanding by absorption of vacancies. The energy of the dislocation ring is constant and depends only on the structural properties of the material. Also, the value of ΔT can be treated as a constant since it is determined by specifics of the crystal growth process. Therefore it is concluded that dislocations are formed in a crystal if the function $S_v=TdC/CdT$, which in the following is called supersaturation, is larger than some critical value $S_{v,c}$. In order to find S_v one needs to know how the vacancy formation energy E_f depends on the doping.

It has been demonstrated recently that the problem of abundances of simple native defects can be quantitatively treated within the concept of amphoteric native defects (AND).[7,8] In the case of GaAs, incorporation of native defects is controlled by the defect reactions

$$\mathrm{As}_{\mathrm{As}}+V_{\mathrm{Ga}}\leftrightarrow V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}} \qquad (2a)$$

and

$$\mathrm{Ga_{As}} + V_{\mathrm{Ga}} \leftrightarrow V_{\mathrm{As}} + \mathrm{Ga_{Ga}} \,. \tag{2b}$$

As has been discussed in Ref. 7, the equilibrium conditions for the reactions (2a) and (2b) are established for the Fermi energy $E_F = E_{\mathrm{FS}}$. The Fermi-level stabilization energy E_{FS} plays an important role of the energy reference for evaluation of the electronic part of the defect formation energy and, as has been shown previously, for GaAs $E_{\mathrm{FS}} \approx E_v + 0.6$ eV for reaction (2a) and $E_v + 0.8$ eV for reaction (2b). This range of E_{FS} agrees very well with the Fermi-level pinning energy at metal-semiconductor interfaces and with the ultimate Fermi-level position in heavily irradiated GaAs.[7] In the following we will discuss the experimental data on GaAs grown under As-rich conditions; therefore we consider the reaction (2a) only. It has to be emphasized that analogous considerations can be applied to Ga-rich GaAs, in which case reaction (2b) is dominant.

In compound semiconductors the formation of dislocations requires the presence of vacancies on both sublattices.[15] In the case of reaction (2a) the condensation of vacancies occurs via the process

$$V_{\mathrm{Ga}} + (\mathrm{As_{Ga}} + V_{\mathrm{As}}) \rightarrow (V_{\mathrm{Ga}} + V_{\mathrm{As}}) + \mathrm{As_{Ga}} \,, \tag{3}$$

where the $(V_{\mathrm{Ga}} + V_{\mathrm{As}})$ pair is absorbed by the dislocation leaving behind excess arsenic in the form of $\mathrm{As_{Ga}}$. The condition for dislocation formation is that the supersaturations for both types of defects V_{Ga} and $(\mathrm{As_{Ga}} + V_{\mathrm{As}})$ are higher than critical supersaturations. The critical supersaturations are determined by the increase of the energy of a dislocation ring expanding via incorporation of V_{Ga} and V_{As}. They depend on the strain energy of the dislocation ring only. Therefore, in the analysis of experimental data we assume that the values of the critical supersaturations are the same for both types of defects and equal to $S_{v,c}$. It has been shown previously[8] that in good approximation the formation energy of V_{Ga} and $\mathrm{As_{Ga}} + V_{\mathrm{As}}$ is $E_f^0 - 3E_F$ and $E_f^0 - 3E_F$, respectively, where E_F is the Fermi energy measured with respect to E_{FS} and E_f^0 is the defect formation energy corresponding to the equilibrium conditions for the reaction (2a). From the definition of supersaturation one obtains

$$S_v = \frac{TdC}{CdT} = \frac{1}{kT}\left[E_f^0 \pm \left(3T\frac{dE_F}{dT} - 3E_F\right) - \frac{TdE_f^0}{dT}\right] , \tag{4}$$

where the sign (+) and (−) corresponds to the V_{Ga} and $\mathrm{As_{Ga}} + V_{\mathrm{As}}$ defect, respectively. The third term in the square brackets contributes to the supersaturation only if a substantial local strain affecting the vacancy formation energy is introduced by the impurities. Doping with EA impurities affects the Fermi energy and can also introduce strain. However, it has been found that suppression of dislocation formation with such impurities is largely independent of the impurity size and its chemical identity[1] and depends only on the type of electrical activity (donor or acceptor). Thus, for EA dopants one can safely assume $dE_f^0/dT = 0$ in Eq. (4).[16]

In order to quantitatively describe the process of dislocation suppression by n- or p-type doping one needs to consider the effect of doping on the supersaturation of V_{Ga} and $(\mathrm{As_{Ga}} + V_{\mathrm{As}})$. In n-type GaAs we have $E_F > 0$ and $dE_F/dT < 0$. From Eq. (4) one finds that S_v is reduced for the V_{Ga} acceptor and enhanced for the $(\mathrm{As_{Ga}} + V_{\mathrm{As}})$ donor. Using similar arguments for p-type doping, with $E_F < 0$ and $dE_F/dT > 0$, one deduces that S_v is reduced or enhanced for $(\mathrm{As_{Ga}} + V_{\mathrm{As}})$ or V_{Ga}, respectively. We infer from the above that to address the dislocation formation one has to consider supersaturation of the majority defects only, i.e., V_{Ga} or $(\mathrm{As_{Ga}} + V_{\mathrm{As}})$ for n- or p-type GaAs, respectively. As is seen from Eq. (4), a knowledge of temperature and doping-dependent Fermi energy is required for a description of supersaturation.

In the presence of native defects the neutrality equation for n-type doped material is

$$n = N_D^+ - 3([D_+] - [D_-]) + n_i^2/n \,, \tag{5}$$

where n_i and n are the intrinsic and free-carrier concentration, respectively, $[D_+] \equiv [V_{\mathrm{Ga}}]$ and $[D_-] \equiv [\mathrm{As_{Ga}} + V_{\mathrm{As}}]$ are concentrations of native defects and N_D^+ is the concentration of shallow donor dopants. Free-carrier and defect concentrations can be expressed in terms of the Fermi energy

$$n = N_c \exp\left(\frac{E_F - E_c}{kT}\right)$$

and

$$D_\pm = C_0 \exp\left(\frac{-E_f^0 \pm 3E_F}{kT}\right) . \tag{6}$$

The Fermi level found by solving Eq. (5) is used in Eq. (4) to determine S_v as a function of temperature and the doping level. The calculations have to be carried out at high temperatures at which dislocations are formed. Most of the GaAs material parameters as well as their temperature dependences are quite well known and are listed in Ref. 17. The value of E_f^0 was adopted to be 5 eV for both GaAs and InP. It should be noted, however, that the results are not strongly dependent on the choice of E_f^0. The parameter C_0 in Eq. (6) depends on the stoichiometry and, as has been shown in Ref. 18, it determines the maximum concentration of free carriers attainable by a given growth technique. The value of C_0 in the present calculation was chosen in such a way that the maximum concentration of free electrons $n \approx 5\times10^{18}$ cm^{-3} for GaAs (Ref. 6) and the maximum hole concentration $p \approx 4\times10^{18}$ cm^{-3} for InP (Ref. 19). These are typical values for the maximum free-electron and hole concentrations in melt-grown GaAs and InP, respectively. The quantities which play an important role in the present calculations and are not known are temperature-dependent energy separations $E_c - E_{\mathrm{FS}}$ and $E_{\mathrm{FS}} - E_v$. The theoretically determined low-temperature value of $E_{\mathrm{FS}} - E_v = 0.6$ eV is in good agreement with experimentally found 0.5 eV $\leq E_{\mathrm{FS}} - E_v \leq 0.7$ eV.[7] There are two effects contributing to the variation of $E_{\mathrm{FS}} - E_v$ and $E_c - E_{\mathrm{FS}}$ with temperature: dilation of the crystal lattice and electron-optical phonon interaction. It has been shown recently[20] that the pressure coefficient $d(E_{FS}-E_v)/dp \approx 0$. This indicates that the lattice dilation affects E_c-E_{FS} only. On the other hand, it can be argued that because the effective mass of holes is larger than that of electrons the temperature-dependent electron-phonon interaction affects mostly the valence-band position. Therefore, one obtains

$$d(E_c-E_{FS})/dT = 3(\Delta a/a)a_c = -2\times 10^{-4}\,\text{eV}\,\text{K}^{-1}$$

and

$$d(E_{FS}-E_v)/dT = d(E_g)/dT - d(E_c-E_{FS})/dT \approx -2.8\times 10^{-4}\,\text{eV}\,\text{K}^{-1}\,.$$

Here, $\Delta a/a$ is the relative temperature-induced change of the lattice constant and dE_g/dT is the temperature coefficient of the energy gap.

The calculated doping dependent supersaturations of majority defects [V_{Ga} for $E_F > E_{FS}$ and ($As_{Ga}+V_{As}$) for $E_F < E_{FS}$] are shown in Fig. 1. It is clearly seen that the supersaturation can be very significantly reduced by doping. In n-type GaAs, S_v is abruptly reduced for donor doping levels exceeding 10^{18} cm^{-3}. Also, a striking difference between n- and p-type GaAs is found. For p-type doping S_v is large even for doping levels as high as 10^{20} cm^{-3}. The characteristic asymmetry reflects the fact that E_{FS} is located in the lower half of the band gap. This, combined with the much lower density of states in the conduction band compared with the valence-band results in much larger doping induced shifts of the Fermi energy in n-type than in p-type material. In general we find that the location of E_{FS} and the density of the band states are the two principal factors which determine how supersaturation is affected by doping. This finding allows for evaluation of the effect of doping on defect supersaturation in other materials. In InP the effect of E_{FS} being located closer to the conduction band[7] ($E_{FS} \approx E_v + 1.0$ eV), is compensated by the higher density of states of the valence band compared to that of the conduction band. Therefore, as is seen in Fig. 1, in this case the effects of p- and n-type doping are much more symmetric. Doping with either acceptors or donors leads to the reduction of supersaturation and thus also to suppression of dislocation formation.

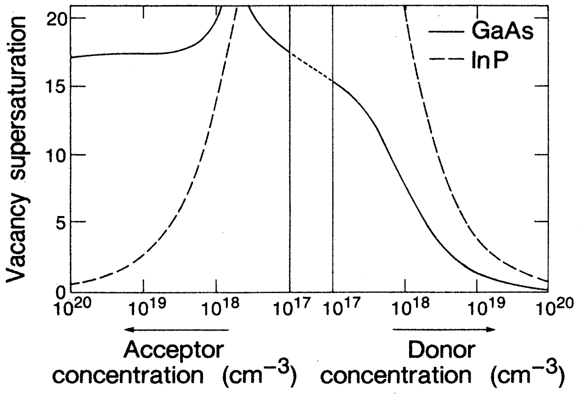

FIG. 1. Defect supersaturations as functions of the doping level. Calculations have been performed for $T=1300$ K (GaAs) and $T=1200$ K (InP).

According to the presently considered mechanism, dislocations are formed if the actual supersaturation exceeds $S_{v,c}$. Although the critical supersaturation is not known, we can test if the present mechanism correctly predicts the trends in dislocation suppression by EA dopants. Results of very extensive studies have shown that in n-type GaAs the threshold doping level for dislocation reduction is $\sim 10^{18}$ cm^{-3} (Ref. 6). One finds from Fig. 1 that this corresponds to $S_{v,c} \approx 8$. Adopting this value of $S_{v,c}$ we find that in p-type GaAs no dislocation suppression is predicted even for the doping level as high as 10^{20} cm^{-3}. On the other hand, for a similar value of $S_{v,c}$ one finds that in InP, p-type doping is very efficient in reducing the supersaturation, and as is seen in Fig. 1 one expects suppression of dislocation formation at a doping level slightly exceeding 10^{18} cm^{-3}. N-type doping of InP is less efficient than p-type, and doping levels of the order of 10^{19} cm^{-3} are required to attain the condition $S_v = S_{v,c}$.

These predicted trends are in very good agreement with experiments where it has been found that doping of GaAs with Zn acceptors has virtually no effect on the dislocation density,[1,21] whereas Zn is the impurity most efficient in reducing dislocation density in InP.[21] A significant reduction of dislocation density in InP doped with Zn to the level of $\sim 10^{18}$ cm^{-3} has been observed.[21] Doping of InP with donors has been reported to be less efficient and slightly dependent on the dopants.[21,22] In any instance doping thresholds for dislocation reduction in the range of 2×10^{18} to 2×10^{19} cm^{-3} were reported.[21,22] This striking agreement of the predictions of our model calculations with experimental data indicates that condensation of vacancies is certainly one of the basic mechanisms of dislocation formation in III-V semiconductors. Complete elimination of dislocations can be achieved by lowering the vacancy supersaturation below $S_{v,c}$. This can be realized only by doping or by low thermal gradient growth of small-diameter crystals in which supersaturation can be lowered by vacancy outdiffusion.

The results in Fig. 1 were obtained for temperatures ~ 200 K below the melting point which were suggested to be relevant to the dislocation formation in GaAs.[1] The choice of the temperature is not critical. As is shown in Fig. 2, for a given doping level of $N_i = 10^{19}$ cm^{-3} we find that the conditions of $S_v < S_{v,c}$ in n-type and $S_v > S_{v,c}$ in p-type material are met over a wide temperature range. This assures that our conclusions are valid independent of the precise temperature at which vacancies begin to condense. The concentrations of free electrons and holes are shown as a function of temperature in Fig. 2. It is seen that the concentration of holes is equal to the concentration of dopants, indicating that the concentration of compensating ($As_{Ga}+V_{As}$) donors is low. For n-type doping the concentration of free electrons does not exceed 5×10^{18} cm^{-3} and is substantially lower than N_i as a result of compensation by V_{Ga}^{3-} acceptors. This once again shows that the previously discussed asymmetry in the limitations of the maximum free-electron and hole concentrations[15] in semiconductors are inherently related to asymmetry in

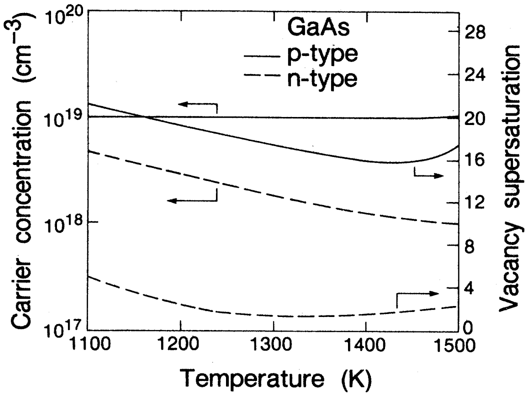

FIG. 2. Defect supersaturations and free-carrier concentrations as functions of temperature for p- and n-type GaAs with $N_A = N_D = 10^{19}$ cm^{-3}.

doping-induced dislocation suppression in n- and p-type GaAs discussed in this paper. In InP the maximum electron concentration is higher than the hole concentration,[16] which is in agreement with the result of the present calculations, showing that p-type doping is slightly more efficient in suppressing dislocation formation than n-type doping.

Within the proposed mechanism of dislocation formation one can now qualitatively understand a number of previous experimental observations. It has been reported that in heavily doped n-type GaAs large concentrations of microdefects are observed.[23] The onset of the microdefect formation correlates with the reduction of dislocation density. This observation can be understood in terms of the present model. For high enough doping $S_v < S_{v,c}$ and dislocation cannot be formed; however, the high number of vacancies which exist in the crystal coalesce to form smaller complexes which are observed as microdefects. Also, since formation of dislocations is associated with gettering of vacancies, the regions around dislocations should be depleted of those defects. This is consistent with experimental data on photoluminescence which have shown that the regions of about 50 to 100 μm around dislocations show photoluminescence intensity orders of magnitude higher than the rest of the crystal.[24] The luminescence contrast was interpreted as resulting from a variation in the nonradiative lifetime of photoexcited carriers, which in turn can be related to variations in concentrations of nonradiative defects. Recent experimental studies have demonstrated that arsenic-rich precipitates and nonstoichiometric defects, e.g., *EL*2 are observed in the vicinity of dislocations.[25] Such observations are consistent with the fact that according to Eq. (3) a process leading to the formation of dislocations leaves a trace of $\mathrm{As_{Ga}}$ defects.

In conclusion, we have proposed a mechanism for suppression of dislocation formation by doping with electrically active impurities. The mechanism is based on the concept of amphoteric native defects. The dislocation suppression results from the Fermi energy-dependent reduction of the defect formation energy and thus also reduction of defect supersaturation. The mechanism explains all the major experimental results in GaAs and InP doped with electrically active impurities.

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