Changes of defect and active-dopant concentrations induced by annealing of highly Si-doped GaAs

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We identified point defects and dopant atoms and measured their concentrations in as-grown and post-growth annealed highly Si-doped GaAs by scanning tunneling microscopy. The annealing under As atmosphere reduces the concentration of Si atoms incorporated into Si pairs and clusters by cluster dissolution, while the concentrations of Si donors, Si donor–Ga vacancy complexes, and Si donor–As vacancy complexes increase. For the dissolution of the Si clusters during heat treatment, a Ga-vacancy-mediated mechanism is suggested. [S0163-1829(98)03408-0]

Compound semiconductor crystals grown under conditions where the doping elements are directly incorporated from the melt, in certain cases, do not exhibit the desired high carrier concentrations in the as-grown state, due to a strong compensation.[1] However, a post-growth heat treatment at elevated temperatures can reduce the degree of compensation and thus lead to a considerable increase of the carrier concentration.[2] Perhaps one of the most prominent examples of this behavior is highly Si-doped GaAs.[3–5] GaAs doped with several 10^{19} cm^{-3} Si atoms reaches in the as-grown state only carrier concentrations of $(1-2)\times10^{18}$ cm^{-3},[6–8] while after heat treatment above about 900 °C the material exhibits carrier concentrations of typically $(5-10)\times10^{18}$ cm^{-3}.[3–6] Although this effect has been known for a long time, the microscopic mechanisms are still not understood. It is well accepted that point defects play a key role, but it is up to now not clear what types of defects are involved and which atomic scale processes take place at high temperatures. Indeed, it is difficult to identify and quantify the defects by means of conventional techniques.[8,9]

In this paper we identify both the defects and the dopant atoms and measure their concentrations in highly Si-doped GaAs before, i.e., in the *as-grown* state, and after heat treatment using atomically resolved scanning tunneling microscope images of (110) cleavage surfaces. We find that during annealing Si clusters are dissolved. At the same time, the concentrations of Si donors, i.e., Si on Ga sites (Si_{Ga}) of complexes consisting of Si on a gallium site and of a Ga vacancy (Si_{Ga}-V_{Ga}) and of complexes consisting of Si on a gallium site and as As vacancy (Si_{Ga}-V_{As}) increase. The concentration of Si_{As} acceptors, i.e., of Si on an As sublattice site, does not change. The results are explained by dissolution of the Si clusters mediated by Ga vacancies (V_{Ga}).

For the experiments we used samples cut from a vertical Bridgeman grown GaAs crystal doped with $(2.5-6)\times10^{19}$ cm^{-3} Si (measured by secondary ion mass spectroscopy, SIMS). One set of samples was annealed at 1130 °C for 2 h under As atmosphere (in order to avoid an As depleted surface) and quenched to room temperature. The carrier concentrations before and after annealing, measured by the Hall effect, were $(1.2-2)\times10^{18}$ cm^{-3} and $(4.5-7)\times10^{18}$ cm^{-3}, respectively (the variations reflect doping inhomogeneities). Both as-grown and annealed GaAs samples were cleaved along a (110) plane in ultrahigh vacuum (5×10^{-9} Pa) and investigated by scanning tunneling microscopy (STM). We measured simultaneously high-resolution constant current images of the occupied and empty states of every type of defect and dopant atom observable in the STM images. This allowed us to identify the defects and dopant atoms unambiguously. From the STM images we determined the concentrations for each defect and for a number of subsurface layers separately. This procedure follows the one described previously for the determination of the concentrations of bulk dopant atoms and defects from STM images.[10–12] It has been shown that the technique yields accurate concentration values of bulk defects, although the STM is basically only a surface sensitive probe.[13]

After cleavage we observed on the *as-grown* GaAs(110) surfaces four types of bulk defects and dopant atoms. These are Si_{Ga} donors, Si_{As} acceptors, Si_{Ga}-V_{Ga} complexes, and Si pairs as well as Si clusters. All these have been imaged and described in Ref. 10, to which we refer for further details. In addition to the four bulk defects we also observed Ga surface vacancies, which were formed after cleavage by Langmuir desorption[10,14] and are therefore not of interest here.

On cleavage surfaces of the *heat-treated* samples we observed the same four types of defect and dopant atoms and one additional type of atomic defect (Fig. 1). This additional defect exhibits one missing occupied dangling bond, but no

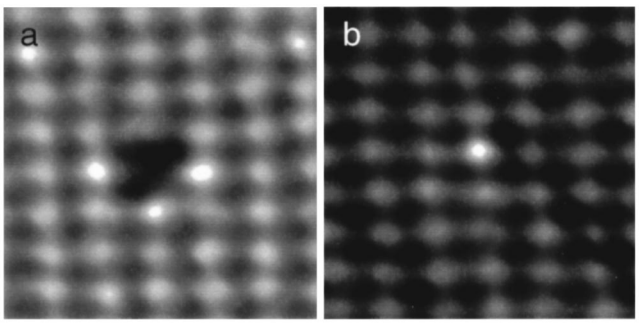

FIG. 1. Occupied (a) and empty (b) density of state images of the defect formed during tempering. The images have been acquired at -2.5 and $+2.2$ V (0.3 nA), respectively. The defect is a Si_{Ga} donor-As vacancy complex (see text).

missing empty dangling bond. No wide elevation or depression is detectable around it. This indicates that the defect is not surrounded by a zone of local band bending. From this we conclude that the defect is electrically neutral. Its concentration does not change with time. Therefore, we conclude that the defect is a bulk defect exposed by cleavage and not formed after cleavage on the surface. The structure of the defect (one missing occupied dangling bond) is very similar to that of P and As vacancies studied on GaP, InP, and GaAs (110) surfaces.[15,16] This suggests that the defect consists of an As vacancy. The defect cannot consist of a Ga vacancy, since no missing Ga dangling bond is observed in the empty-state images. Furthermore, it was observed in Ref. 10 that, after cleavage of *n*-type GaAs, the concentration of all types of V_{Ga} related defects increases with observation time due to the mentioned Ga surface vacancy formation. This is not observed for the defect shown in Fig. 1. However, the defect cannot consist of an isolated As vacancy. For an isolated uncharged V_{As} a fully symmetric structure is expected.[16] The defect exhibits, however, a pronounced asymmetry in the occupied states along the atomic chains [compare the depressed occupied dangling bond above the missing dangling bond in Fig. 1(a) with the raised dangling bond below the missing dangling bond]. Furthermore, only one empty dangling bond is raised. For an isolated monovacancy two equally raised (or affected) neighboring dangling bonds have been observed[15] and predicted.[17,18] This suggests that the defect is not an isolated As vacancy but rather a complex consisting of an As vacancy and some other partner. In order to identify the second constituent we have to take its electrical charge into account. An isolated As vacancy is expected to be single negatively charged on *n*-doped GaAs(110) surfaces.[18] The complex is, however, uncharged. Thus the other contribution to the complex must be a positively charged donor. In Si-doped GaAs only Si_{Ga} is a donor. With the assumption of a Si_{Ga}-V_{As} complex the raised empty dangling bond can be understood to indicate the location of the Si atom. The asymmetry of the complex is the signature of its dipole character in agreement with previous observations of Si_{Ga}-V_{Ga},[10] Zn_{In}-V_P,[19] and Zn_{Ga}-V_{As} (Ref. 20) complexes. Therefore we conclude that we observed in the annealed GaAs samples a Si_{Ga}-V_{As} complex. The discussion below will provide further support for this interpretation.

During heat treatment, the defect concentrations change significantly. Figure 2 shows the defect concentrations measured from the STM images of the as-grown and annealed samples. We find that, during annealing, the concentration of Si incorporated in Si clusters, Si_n, drops by nearly one order of magnitude. In absolute terms this means that the Si clusters are nearly entirely dissolved. This observation is in agreement with transmission electron microscopy results.[21] The concentration of Si_{Ga} donors increases by about 5×10^{18} cm^{-3}, while the concentration of Si_{As} acceptors remains essentially constant. Furthermore, the concentration of Si_{Ga}-V_{As} complexes increases as they were not observed in measurable concentrations on as-grown samples. Finally, we also find a slight increase of the concentration of Si_{Ga}-V_{Ga} complexes. However, since we cannot exclude an effect of the Langmuir-desorption induced surface Ga vacancies,[10,13] we shall exclude this observation from our further discussion. The total concentration of Si remains constant. The

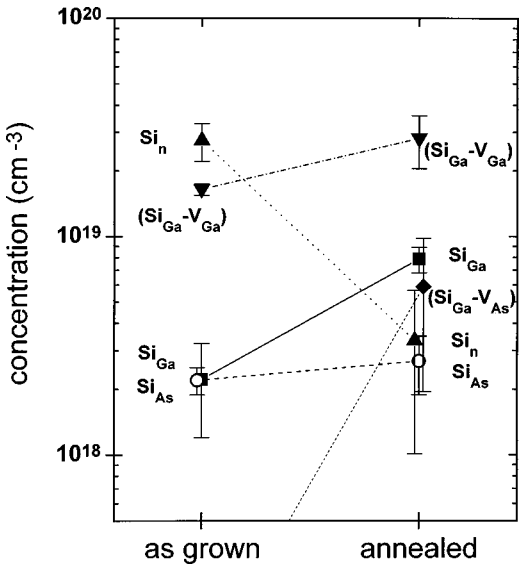

FIG. 2. Concentration of Si incorporated in different defects in the as-grown and in the annealed GaAs crystal. The lines connecting the points should guide the eye. Si_{Ga}, Si_{As}, ($Si_{Ga}-V_{Ga}$), Si_n, and ($Si_{Ga}-V_{As}$) refer to Si donors (■), Si acceptors (○), Si donor–Ga vacancy complexes (▼), Si pairs and clusters (▲), and Si donor–As vacancy complexes (♦), respectively.

STM measurements, $(4.7\pm1)\times10^{19}$ cm^{-3} and $(4.8\pm1)\times10^{19}$ cm^{-3} for the as-grown and annealed GaAs, respectively, agree with the Si concentration measured by SIMS.

At this stage we correlate the increase of the carrier concentration during annealing with the observed concentration changes of the defects and dopants. During annealing the carrier concentration increased between 2.5×10^{18} and 6×10^{18} cm^{-3} depending on the local Si concentration. The observed increase of the concentration of Si_{Ga} donors by 5×10^{18} cm^{-3} agrees well with the increase of the carrier concentration. This suggests that the increase in the carrier concentration is due to the dissolution of Si clusters into isolated Si_{Ga} donors. Also the data in Fig. 2 provide us with a basis to deduce the microscopic processes leading to the increased carrier concentration. Three key facts need to be considered. First, Si clusters are dissolved only into Si_{Ga} donors, but not into Si_{As} acceptors. Second, Si_{Ga}-V_{As} complexes are produced but no Si_{As}-V_{Ga} complexes. Finally, the Si concentration remains constant.

For the following discussion we have to recall that at elevated temperatures the defects do not only become mobile, but also their equilibrium concentrations change. In highly *n*-doped GaAs only Ga vacancies are stable, occur in high concentrations, and are mobile at elevated temperatures.[22] This is due to the Fermi-level effect which favors Ga vacancy formation.[23,24] Theoretical calculations also show that under As rich conditions the Ga vacancy has the lowest formation energy in *n*-doped GaAs.[25,26] Thus the basis for all defect reactions at high temperature is the existence of mobile Ga vacancies. If a Ga vacancy reaches a Si pair or cluster, one Si atom can jump into the vacant Ga site. This jump can be either performed by a Si atom on a Ga site or on an As lattice site. It is described by

$$(Si_{Ga}\text{-}Si_{As})+V_{Ga}\rightarrow(Si_{As}-V_{Ga})+Si_{Ga} \quad (1)$$

and

$$(Si_{Ga}\text{-}Si_{As})+V_{Ga}\rightarrow(Si_{Ga}\text{-}V_{As})+Si_{Ga}, \quad (2)$$

respectively. Both Si extraction processes from aggregates lead to one additional Si_{Ga} donor but not to an isolated Si_{As} acceptor. Both processes form also a Si-vacancy complex. This complex allows us to discriminate which one of the two jump processes is more likely to occur. The first equation involving a jump of a Si_{Ga} predicts the formation of a $(Si_{As}\text{-}V_{Ga})$ complex, while the second equation leads to $(Si_{Ga}\text{-}V_{As})$ complexes. Since we could only observe $(Si_{Ga}\text{-}V_{As})$ complexes but no $(Si_{As}\text{-}V_{Ga})$ complexes, only the second type of jump process is supported by our data. Such a jump appears also favorable on the basis of the fact that a Si atom on an As lattice site is a direct neighbor of a Ga vacancy site, whereas a jump of a Si on a Ga site is a second neighbor jump. Also the charge effects are in favor of this process. The Ga vacancy is expected to have a triple negative charge.[24,27] Thus the complex consisting of a negatively charged Si_{As} acceptor and a Ga vacancy has four electron charges. Such a high charge is unlikely to be stable. On the other hand, a positively charged Si donor compensates a single negatively charged As vacancy.[27–32] This compensation is expected to increase the stability of the complex. The increased stability is in agreement with the observation of the formation of uncharged complexes due to the attractive Coulomb interaction.[19]

It should be noted that As vacancies are not expected to be stable under equilibrium conditions in *n*-type GaAs since the formation energy is much higher than that of Ga vacancies.[27] Their observation in a complex thus points out the importance of the charge compensation. The newly formed Si_{Ga} donors as well as the complexes should be able to migrate away from the cluster. It has been suggested that the diffusion in *n*-type GaAs is a Ga vacancy dominated diffusion process.[22–24]

The main result of the dissolution of the Si clusters by Ga vacancies is the formation of Si_{Ga} donors and Si_{Ga}-V_{As} complexes in equal concentrations. Si_{As} acceptors are not formed. This agrees very well with the data in Fig. 2 and we will show below that the model is supported by the observed defects and their concentrations. First, the concentration of isolated Si_{As} acceptors remains unchanged. This excludes a simple dissolution of Si clusters by a migration of Si donors and Si acceptors without Ga vacancies and without the possibility of a sublattice change of Si. This would only lead to isolated Si donors and Si acceptors in comparable concentrations and therefore not to an increase of the carrier concentration. Second, the presence of Si_{Ga}-V_{As} complexes in concentrations of about $(5-6)\times10^{18}$ cm^{-3} agrees with the observed increase of the concentration of Si donors of about 5×10^{18} cm^{-3}, which can be taken as strong support of our model. The increase of the concentration of Si_{Ga}-V_{Ga} complexes can be understood in terms of the Fermi-level effect favoring the formation of Ga vacancies.

The occurrence of Si_{Ga}-V_{As} complexes in high concentrations allows us to conclude that these must be uncharged inside the GaAs crystal. If they were charged they would counteract the effect of the increased Si donor concentration on the carrier concentration. This is not observed. The complexes are also uncharged on the surface. Thus the isolated As vacancy is single negatively charged on the surface as well as in the bulk of *n*-doped GaAs. This agrees with calculations of surface As vacancies[18] and measurements of surface P vacancies on *n*-doped InP(110),[16] as well as with the results of positron annihilation experiments probing bulk As vacancies.[29,30]

The observation of a Si_{Ga}-V_{As} complex may help to settle the issue concerning the microscopic origin of the so-called Si-*Y* and Si-*X* lines in local-vibrational-mode spectra.[4,33] In Ref. 10 it could be shown by STM that one of the two complexes (the one called Si-*Y* in Ref. 33) is a Si_{Ga}-V_{Ga} complex. Here now we suggest that the defect called Si-*X* in Ref. 33 is a Si_{Ga}-V_{As} complex, because this is the only Si containing defect observed and not yet attributed to any of the features in local vibrational mode spectra. Both complexes are preferentially observed in annealed Si-doped GaAs,[4] in agreement with the trends visible in Fig. 2.

In conclusion, we determined the types of atomic defects and their concentrations in as-grown and tempered highly Si-doped GaAs using atomically resolved scanning tunneling microscopy images. We observed a dissolution of Si clusters and a corresponding increase of the concentration of Si donors, of Si_{Ga}-V_{Ga} complexes, and of Si_{Ga}-V_{As} complexes. The concentration of Si acceptors remains constant. The defect concentrations are explained using a V_{Ga}-dominated dissolution of Si clusters. This mechanism allows Si to change from As to Ga sublattice sites.

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