Direct observation of precipitates and self-organized nanostructures in molecular-beam epitaxy grown heavily doped GaAs:Si

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(Received 8 May 1995; accepted for publication 11 September 1995)

We report a cross-sectional scanning tunneling microscopy investigation of heavily Si doped [001]-oriented GaAs grown by molecular-beam epitaxy. At a very high doping level (6 \times 10^{19} \text{ cm}^{-3}), Si-doping induced precipitates are directly observed in XSTM images of the as-grown epitaxial layers. Most of the precipitates are found to have a characteristic oval shape with the long axis (\sim 80 \text{ Å}) along the growth direction. In contrast to the low diffusivity of randomly distributed Si dopants in the moderate doping regime, these precipitates are found to be highly mobile and spontaneously form “nanowires” during crystal growth. © 1995 American Institute of Physics.

The ability to dope compound semiconductors with high carrier concentrations and ambipolar doping types is crucial for the development of optoelectronic and high speed electronic device technology. Recent breakthroughs in doping \textit{p}-type ZnSe and GaN for light-emitting devices are the most notable examples. However, despite the technological advances, the microscopic origins of the difficulties in doping compound semiconductors are still under current debate. In the case of commonly used Si doping of molecular-beam epitaxy (MBE) grown GaAs(001), almost all the Si dopant atoms occupy the Ga atom sites (Si\text{Ga}) and act as electrically active donors at moderate doping concentrations. However, the free carrier concentration is limited to about 5 \times 10^{18} \text{ cm}^{-3} and drops drastically with increased Si concentrations, which indicates that some form of compensation mechanism dominates at high doping concentrations. Several models have been proposed for the doping behavior of Si dopants in the heavily doped regime. For example, the auto-compensation model based on the amphoteric nature of Si dopants suggests that some Si atoms substitute the As atom sites at high doping levels and act as acceptors. Alternative compensation mechanisms based on the formation of electrically inactive Si complexes, Si\text{Ga}–Si\text{As} pairs, or Si–X (X: some unknown native defects) complexes have also been proposed. In all cases, an experimental approach to provide a direct view of microscopic doping properties in compound semiconductors has become increasingly important.

Recently, cross-sectional scanning tunneling microscopy (XSTM) has been successfully developed to study III-V semiconductor heterostructures with unprecedented spatial resolution in both lateral and vertical directions. In typical XSTM studies of III-V semiconductors grown on (001) substrates, observations were performed on postgrowth cross-sectional (110) surfaces of epilayers prepared by \textit{in situ} cleaving of the samples. At moderate doping levels, it has been shown that electrically active dopant atoms can be imaged as bright spots superimposed on the GaAs lattice image of the unreconstructed (110) surface in the constant tunneling current mode. Moreover, dopant atoms at these levels have been found to be randomly distributed. In this work, by using XSTM technique on heavily Si-doped GaAs epilayer samples, we have found that the doping behavior is quite different as compared with moderately doped cases. Here we present the first direct observation of Si-doping induced precipitation and novel self-organized nanostructured precipitates at a very high doping level.

The Si-doped GaAs epilayers used in our studies were grown by MBE on \textit{p}-type Zn-doped (1 \times 10^{19} \text{ cm}^{-3}) GaAs(001) substrates. The growth rate was approximately 1.2 \text{ μm} per hour and the growth thickness of the GaAs:Si epilayer was 3.6 \text{ μm}. A low growth temperature (375 °C) and a high As/Ga flux ratio (20:1) were used during MBE growth to increase the silicon doping efficiency. The Si concentration was determined to be 6 \times 10^{19} \text{ cm}^{-3} by secondary ion mass spectroscopy (SIMS). The as-grown epilayer samples were cleaved in ultrahigh vacuum (UHV) and transferred \textit{in situ} into an UHV STM chamber for measurements on the (110) cross-sectional cleavage surfaces. The base pressure of this multichamber system during the experiments was better than 1 \times 10^{-10} \text{ Torr}. Both electrochemically etched tungsten tips and mechanically ground platinum tips were used in the experiments. All XSTM images presented here were obtained in the constant current mode at a sample bias of +2.0 \text{ V} and a tunneling current of 0.5 nA.

Shown in Fig. 1 is an XSTM image obtained at the interface formed between the heavily Si-doped GaAs epitaxial layer and Zn-doped GaAs substrate. In this image, the cleavage surface in the substrate region is atomically flat with only a few straight step edges of one- or two-atomic-layer height. On the contrary, the cleavage surface in the epilayer region is very rough, evident by the presence of a striped structure of high density meandering cleavage steps. Furthermore, the abrupt change in the cleavage property appears to...
Higher than the typical growth temperatures.

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senic precipitation can be ruled out in our samples for two reasons. First, the growth temperature of our samples is always multiples of atomic layer height (2 Å). In our observations, most of these protrusions showed a characteristic asymmetric shape with the long axis (~80 Å) along the [001] growth direction and the short axis (~25 Å) along the [110] direction. The fact that the orientation of these protrusions differs from that of the striped cleavage step structure strongly indicates the observed protrusions were not created in the cleavage process. Active dopants and impurities other than Si can be ruled out as sources for these protrusions since only a tiny fraction of Si atoms were active dopants in this doping regime and there was no other measurable impurities except Si dopants in the epilayer. Thus, we conclude that the most plausible origin of these protrusions shown in the XSTM images should be Si-doping induced precipitates formed during MBE growth.

Arsenic precipitates in low-temperature-grown (LT) and annealed GaAs and carbon precipitates formed in heavily doped GaAs:C and InP:C have also been found using XSTM and Raman spectroscopy techniques, respectively. Arsenic precipitation can be ruled out in our samples for two reasons. First, the growth temperature of our samples is higher than the typical growth temperatures (200–300 °C) for LT-GaAs, which is known to contain an excess arsenic concentration in the form of AsGa antisite point defects. Second, arsenic precipitation occurs only after postgrowth annealing of LT-GaAs at 500–900 °C while in our study the samples are as-grown. Nevertheless, the detailed structure of these Si-doping induced precipitates, e.g., the chemical composition and the lattice locations of Si atoms, would require more detailed spectroscopic investigation.

In our XSTM observations we have found that, unlike individual Si dopants which diffuse very slowly, these precipitates are highly mobile and easily form lower energy configuration structures. At the initial stage of MBE growth, the precipitates cannot form any particularly ordered structure since the initial growth front is rough as indicated by a spotty reflection high-energy electron diffraction (RHEED) pattern. As the growth front becomes smoother nanostructured precipitates with high degree of ordering begin to form. In Fig. 2, which is an XSTM image near the central part of the epilayer region, we can observe this unexpected formation of the precipitated “wires” or “plates” (depending on the depth of these structures in the [001] direction). Due to the surface sensitive nature of STM measurements, we are unable to determine the exact depth of each precipitated “wire.” Occasionally, we could observe the three-dimensional structure of these “wires” in the first few layers at the surface. Shown in Fig. 3 is such an example in which we can observe the close-packed stacking of precipitates located at different atomic layers.

The most remarkable structural features of the heavily Si-doped GaAs shown in Figs. 2 and 3 are the uniform size and shape of Si-doping induced precipitates and the self-organized formation of nanostructured precipitates in the (001) growth plane. The characteristic asymmetric shape (with the long axis along the [001] growth direction) of precipitates indicates that the formation mechanism of precipitates may probably be related to a strain relaxation process in growing heavily Si-doped GaAs since Si dopants incorporate on top of the previously deposited Si sites on the growing
nanostructures reside exactly in the spontaneously formed nanostructured precipitates, these and thus minimize the number of the strained bonds. As for the boundary area between precipitates and the host material such a structure the aggregation of precipitates greatly reduce Figs. 2 and 3 also supports the above argument because in theics. The closed-packed structure of precipitates observed in of precipitates is determined by the growth rate and dynam-
surface is energetically more favorable. In this case, the size of precipitates is determined by the growth rate and dynamics. The closed-packed structure of precipitates observed in Figs. 2 and 3 also supports the above argument because in such a structure the aggregation of precipitates greatly reduce the boundary area between precipitates and the host material and thus minimize the number of the strained bonds. As for the spontaneously formed nanostructured precipitates, these nanostructures reside exactly in the (001) plane, indicating that the precipitates tend to segregate on the growth front Thus one possible mechanism for the formation of nanostructured precipitates is that precipitates continue to accumulate on the surface during growth until reaching a critical surface concentration and then “freeze-in” the observed structures. In this model, we can then roughly estimate the diffusion constant of precipitate along the growth direction. By using the simple relation of \( I = (D \tau)^{1/2} \), where \( I \) is the average separation (1000 \( \AA \)) of the “wires” or “plates” along the growth direction, \( \tau \) is the formation time (300 s, the growth time for 1000 \( \AA \) GaAs), and \( D \) is the diffusion coefficient of the precipitates along the growth direction, the minimum diffusion coefficient \( D \) required for forming such precipitated “wires” or “plates” is found to be about 3.3 \( \times 10^{-13} \) cm²/s. This number is several orders of magnitude larger than the diffusion coefficients of Si dopants at moderate doping levels (as a comparison, \( \sim 3.0 \times 10^{-18} \) cm²/s at 600 °C).\(^\text{14}\) Concentration-dependent rapid diffusion of Si atoms in heavily doped GaAs:Si has also been reported in the literature.\(^\text{15,16}\) This phenomenon was previously concluded as due to the \( \text{Si}_{\text{Ga}} - \text{Si}_{\text{As}} \) compensating pairs which have a larger diffusion coefficient.

In summary, we have studied the microscopic doping behavior of heavily doped GaAs:Si using XSTM. The Si-doping induced precipitation was observed directly by XSTM. These precipitates were found to have a characteristic asymmetric shape and were highly diffusive. We suggest that the highly diffusive behavior of Si atoms in heavily doped GaAs:Si reported earlier is closely related to the existence of these precipitates. In our studies, we also found a novel phenomenon of self-organized formation of nanostructured precipitates.

The authors would like to thank Dr. T. D. Harris, Dr. I. Fujimoto, and Dr. L. A. Nagahara for helpful discussions. This work was supported by the New Energy and Industrial Technology Development Organization (NEDO).