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Description	

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Influence of electronic states on precipitation of metallic As clusters in LT-GaAs

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The influence of electronic states of the semiconductor matrix on the precipitation of metallic As clusters in GaAs epilayers grown by molecular beam epitaxy at low temperatures were studied. From x-ray diffraction and Hall effect measurements, the presence of free carriers was found to occur in a certain time after the start of the coarsening stage of the precipitation. Transmission electron microscope observations indicate that redistributions of As clusters between the doped and undoped regions starts at the same time with the appearance of free carriers. Redistributions of As clusters occurs in *pn* junction structures in such a way that depletion zones of the *pn* junctions become free from As clusters, leading to close correlation of widths of precipitate free zones with those of the depletion zones of the *pn* junctions for various dopant concentrations. These observations are explained with a tendency of As metal clusters of reducing free carriers in the surrounding semiconductor matrix and hence keeping it as an intrinsic semiconductor. © *2000 American Institute of Physics.* [S0021-8979(00)01523-1]

I. INTRODUCTION

The growth of GaAs by molecular beam epitaxy (MBE) at a low temperature around 200 °C under the arsenic-rich flux condition results in a highly nonstoichiometric composition of the epilayer (LT-GaAs) with excess arsenic in the GaAs matrix.[1] The excess arsenic is incorporated in the form of point defects, mainly, as As antisites.[2] The incorporation of excess As gives rise to the increase of lattice spacings, but the epilayer remains pseudomorphic with high structure perfection. Upon annealing, excess arsenic forms As clusters while the GaAs matrix changing towards a stoichiometric crystal.[3] With transmission electron microscope observations, As clusters have been identified as the rhombohedral phase which is known as metallic.[3] Because of the high concentration of excess As, LT-GaAs exhibits a number of novel properties such as extremely high electrical resistivity upon annealing[4] and ultrashort lifetime of photoexcited free carriers.[5] Two models have been proposed for explanation of the origin of these novel properties. The one model attributes the properties to As point defects,[6] and the other to As precipitate clusters.[7]

When As metal clusters form in the *n*-or *p*-type semiconductor matrix, conduction electrons or holes, i.e., free carriers are expected to be transferred from the surrounding matrix to the clusters. The transfer of free carriers results in the formation of internal Schottky barriers at the cluster–matrix interfaces and, hence, depletion zones around precipitate clusters. Depletion zones overlap one another in the early stage of annealing where the number density of precipitate clusters is high, and, therefore, result in the high electrical resistivity. Metallic clusters are also expected to serve as very efficient recombination sites of photoexcited carriers, resulting in their ultrashort lifetime. Up to the present, the existence of internal Schottky barriers and hence depletion zones around As clusters in annealed LT-GaAs have been observed by scanning tunneling microscope (STM)[8] and internal photoemission experiments.[9]

Because of the fundamentally interesting nature of this internal Schottky barrier around a metal cluster and also the important role of As clusters in the novel properties of LT-GaAs, it is desirable to further clarify the formation process of As metal clusters and their Schottky barriers. Although numerous studies of LT-GaAs have been carried out in the past, it has not been clarified at what stage of the precipitation As clusters start to act as metal clusters and incorporate free carriers from a surrounding semiconductor matrix. The transfer of free carriers from the semiconductor matrix to metallic precipitate clusters also implies a possibility of direct influence of free carrier distributions on the precipitation process of clusters. Earlier transmission electron microscope (TEM) observations have shown strong influence of the presence of electrically active impurities, i.e., Si and Be, on the precipitation process of excess arsenic.[10,11] Among those observations, the lack of As precipitates in *pn* junction regions may have resulted from direct influence of free carrier distributions, because at the *pn* junction region free carriers are depleted due to the band bending while doped impurities being uniformly distributed.

In this article we report a series of experiments which were aimed at clarifying the influence of the electronic states of the surrounding semiconductor matrix on the precipitation process of As clusters. The experimental observations have

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clearly shown that the influence begins to occur when free carriers start to appear in the surrounding semiconductor matrix. From the experiments of *pn* junction structures, we also obtained solid evidence that As clusters incorporated both conduction electrons and holes from the surrounding GaAs matrix.

II. EXPERIMENTAL PROCEDURE

LT-GaAs structures were grown by utilizing conventional MBE systems. The one structure consists of an undoped LT-GaAs layers and a Si doped LT-GaAs layers each of which has a thickness of 760 nm. The undoped layer was first grown, and the doped layer was grown with a Si concentration of $1\times10^{18}\,\mathrm{cm}^{-3}$ directly on the undoped layer. The growth temperature of both layers was 240 °C, and the growth rate 0.76 μm/h. The As_4 flux was used with the flux ratio of As_4/Ga being 40 in the beam flux monitor (BFM) reading. The other structure was *pn* junction structures with three periods of a Si doped layer and a Be doped layer each of which has 200 nm. The growth temperature was 250 °C and the growth rate was the same as used for the other two layer structure. Three *pn* junction structures were grown with dopant concentrations of 3.5×10^{18}, 1.0×10^{18}, and $4.0\times10^{17}\,\mathrm{cm}^{-3}$, respectively. The flux condition was the same as used for the other structure, except for the *pn* junction structure with the dopant concentration of $1.0\times10^{18}\,\mathrm{cm}^{-3}$ for which the As_2 flux was used instead of the As_4 flux.

The annealing of a LT-GaAs structure were carried out in a nitrogen flow. For each annealing, a sample was inserted from the position kept at room temperature to that kept at the annealing temperature and pulled it out to the initial position at the end of the annealing. X-ray diffraction measurements of as-grown and annealed samples were carried out by utilizing a x-ray diffractometer with a four crystal monochrometer. Free carrier concentrations in the annealed samples were estimated by the Hall effect measurement with the van der Pauw method for which an In contact were made at each corner of the sample. A cross sectional sample for TEM observations was made in the standard procedure. TEM observations of As clusters were carried out in the bright field imaging mode.

III. RESULTS AND DISCUSSION

A. Doped and undoped two-layer structure

The annealing of small samples with a 5 mm×5 mm size was done at 750 °C for different periods, and each annealed samples were measured by x-ray diffraction. Figure 1 shows 400 x-ray rocking curves of the samples annealed for 5, 15, 30, and 60 s, respectively, along with that of the as-grown sample. The figure shows that, with the progress of the annealing, a peak of the LT-GaAs layer in the left-hand side moves towards the peak of the GaAs substrate and only a single peak is observed after the 30 s annealing. The peak of the sample annealed for 60 s is narrower than that of the sample annealed for 30 s. Although results are not shown in this figure, rocking curves of the samples annealed for periods longer than 60 s appear identical to that of the sample annealed for 60 s, implying that the GaAs matrix remains unchanged by the annealing for more than 60 s.

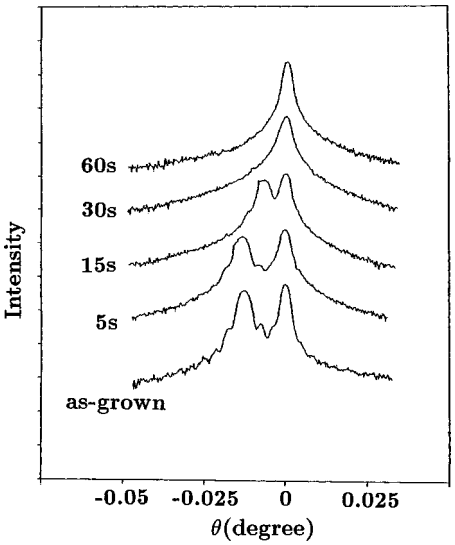

FIG. 1. X-ray rocking curves of 400 reflections of as-grown and annealed of two layer structures.

The results shown in Fig. 1 indicate that the GaAs crystal contains excess As as a form of point defects up to the 30 s annealing, while As clusters keep growing by incorporating excess As atoms from the surrounding GaAs crystal during this annealing period. At the 60 s annealing almost all excess As in the GaAs crystal have been extracted as a form of As clusters, and the precipitation process enters its coarsening stage where redistribution of As clusters are taking place. A Hall effect measurement of the sample annealed for 60 s showed no free carrier in this sample. In Fig. 2(a) is a cross sectional TEM image of the sample annealed for 60 s. The

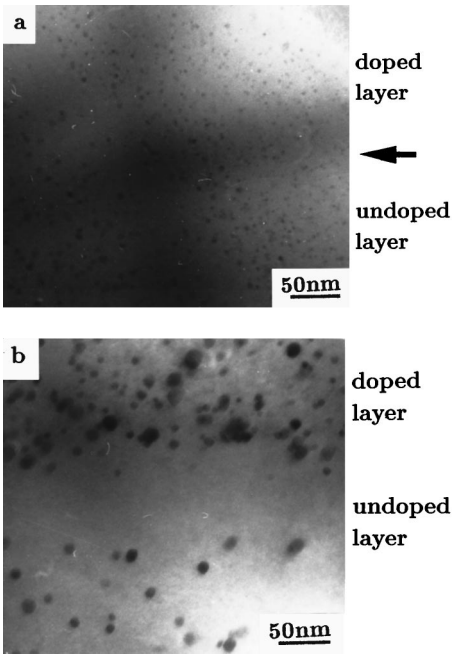

FIG. 2. Cross-sectional TEM images of the doped and undoped two layer structure. The images (a) and (b) were taken from the sample annealed at 750 °C for 60 s and 15 min, respectively.

image was taken from the region of the boundary between the undoped and doped layers. As clusters with diameters of several nanometers are uniformly distributed over the boundary region, showing that no significant redistribution of As clusters has occurred between the two layers. This uniform distribution of As clusters in both doped and undoped regions also indicates that the presence of dopant impurity atoms, that is, Si atoms, has no significant effect on the nucleation of As clusters in LT-GaAs crystal.

The presence of free carriers were observed from samples annealed for periods longer than a few minutes. Figure 2(b) is a cross-sectional TEM image of the boundary region of the sample annealed for 15 min. From the Hall effect measurement, a free carrier concentration in the doped layer of this sample was estimated to be $8.0\times10^{17}\,\mathrm{cm}^{-3}$. In the TEM image, a region in the undoped layer side of the boundary is seen to be free from As clusters, which may be called a precipitate free zone. The width of this precipitate free zone is approximately 90 nm. The image also shows that the doped layer side of the boundary has a higher concentration of As clusters than those in the interior region of the doped layer, indicating that redistribution of As clusters has occurred from the undoped layer side to the doped layer side.

Results of the doped and undoped two layer structure indicate that the coarsening stage of precipitation of As clusters begins in about 1 min after the start of the annealing at 750 °C. Free carriers, that is, conduction electrons in the present case, starts to appear in the doped layer a few minutes after the start of the coarsening stage, although the surrounding GaAs crystal has nearly no excess As atoms at the coarsening stage. This implies that the lack of free carriers in the early stage of the coarsening stage results from the incorporation of charge carriers by metallic arsenic clusters. The TEM observations shown in Fig. 2 also suggest that redistribution of As clusters from the undoped region to the doped region may have occurred under the condition that free carriers are present in the doped region.

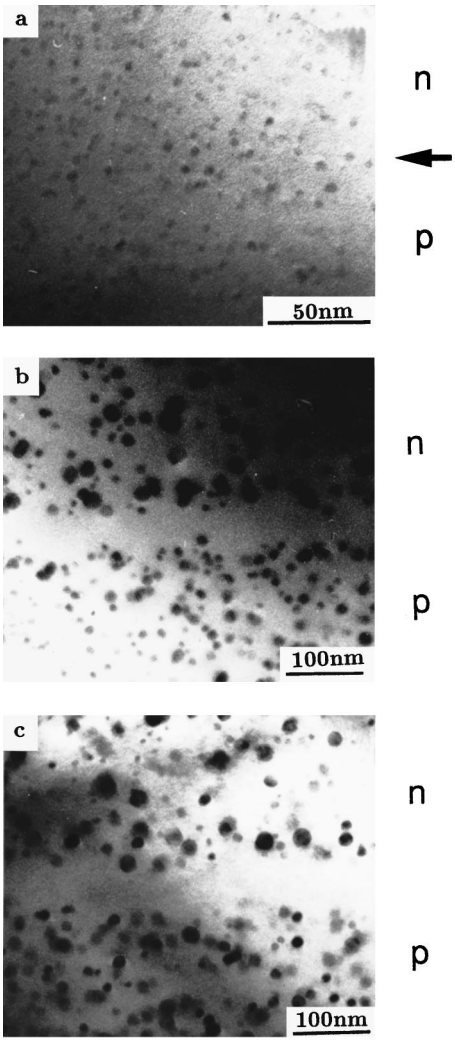

FIG. 3. Cross-sectional TEM images of the *pn* junction structure doped with $3.5\times10^{18}\,\mathrm{cm}^{-3}$ Si and Be. Images (a), (b), and (c) were taken from the samples annealed at 750 °C for 45 s, 5 min, and 60 min, respectively.

B. *pn* junction structures

Three *pn* junction structures, whose Si and Be concentrations are 3.5×10^{18}, 1.0×10^{18}, and $4.0\times10^{17}\,\mathrm{cm}^{-3}$, were annealed at 750 °C and examined by cross sectional TEM. From the TEM observations, it was found that precipitate free zones developed at the *pn* junction regions with the progress of annealing. Figure 3 shows this development of a precipitate free zone by the annealing. The sample has a dopant concentration of $3.5\times10^{18}\,\mathrm{cm}^{-3}$. From Figs. 3(a), 3(b), and 3(c) whose annealing times are 45 s, 5 min, and 60 min, respectively, it is seen that As clusters have uniformly formed in the beginning, and the precipitate free zone has started to develop in a few minutes of the annealing. The uniform distribution of As clusters in Fig. 3(a) implies that there is no significant effect of the difference of doped impurities, that is, Si and Be, on the nucleation of As clusters. As observed from the doped and undoped two layer structure, redistribution of As clusters has started in a certain time after the beginning of the coarsening stage of the precipitation. The most important observation made from these TEM images is the steady state width of the precipitate free zone; the width has remained unchanged from 5 min annealing to 60 min annealing despite an increase of the size of As clusters. If the formation of the precipitate free zone was induced by interdiffusion of Si and Be atoms across the junction, the width was expected to keep increasing with the annealing time. The similar observations with respect to the width of the precipitation free zone were made from the other two *pn* junction structures. The constant width of the precipitate free zone suggests that the width is determined by an energetic factor rather than by a kinetic factor. In other words, the precipitation free zone is not a transitional structure which eventually changes to another form of a structure.

Next we compare widths of precipitate free zones of three *pn* junction structures in order to examine their dependence on the dopant concentration. Figure 4 is a TEM image of precipitate free zones in three *pn* junction structures. The images were taken from the samples annealed for 60 min where the widths of precipitate free zones have become constant as seen from Fig. 3. The TEM images in Fig. 4 show a clear correlation of the width of the precipitate free zone with

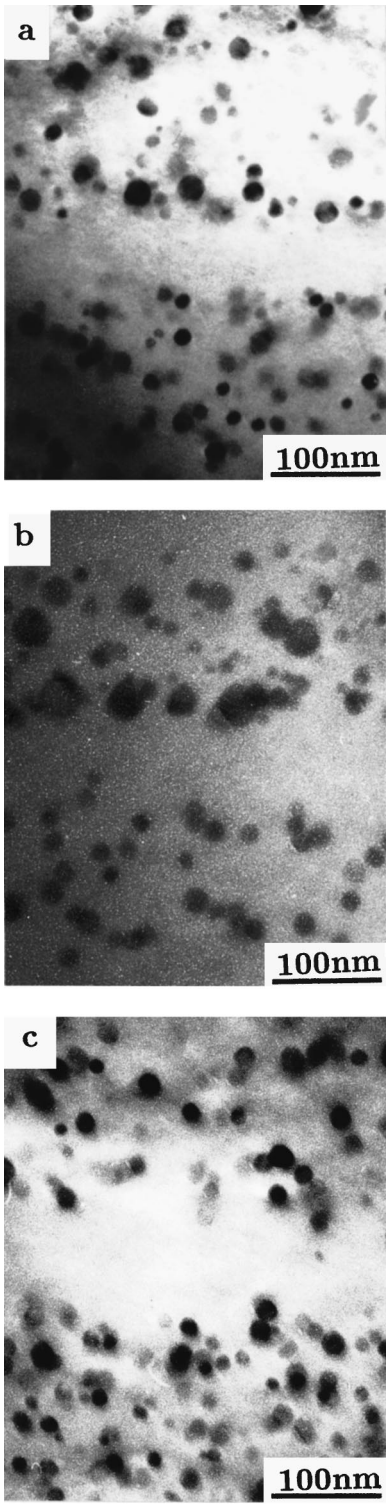

FIG. 4. Cross sectional TEM images of *pn* junction structures annealed at 750 °C for 60 min. Images (a), (b), and (c) were taken from *pn* junction structures with dopant concentrations 3.5×10^{18}, 1.0×10^{18}, and $4.0\times10^{17}\,\mathrm{cm}^{-3}$, respectively.

the dopant concentration. As the dopant concentration becomes lower, the width of the precipitation free zone increases. According to rough estimation from TEM images, the average widths of the precipitate free zone in *pn* junction structures doped with 3.5×10^{18}, 1.0×10^{18}, and $4.0\times10^{17}\,\mathrm{cm}^{-3}$ are 60, 75, and 95 nm, respectively. Because As clusters at the edges of the precipitate free zones are not aligned along straight lines, the width of the precipitated free zone in each sample varies by ±10 nm from the abovementioned average values.

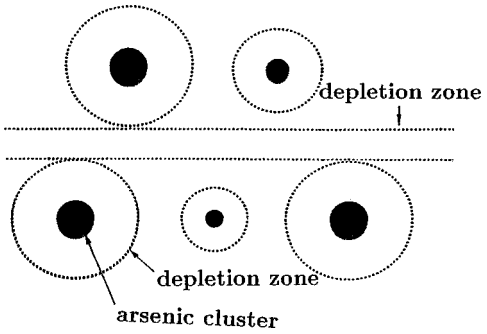

FIG. 5. Arrangement of As clusters at a *pn* junction giving rise to a precipitate free zone. A depletion zone of each As cluster is located on the outside of the depletion zone of the *pn* junction.

The correlation between the width of the precipitate free zone and the dopant concentration suggests a novel mechanism underlying the development of the observed microstructures. If the formation of the precipitate free zone at the *pn* junction results from direct interaction of As clusters with dopant impurity atoms such as segregation of impurity atoms at cluster interfaces, the width is expected to increase as the dopant concentration is higher, which is exactly opposite to the present case. There is only one mechanism which can explain the observed correlation. It is known that the carrier depletion zone of a *pn* junction becomes wider as the dopant concentration is set lower. For the dopant concentrations 3.5×10^{18}, 1.0×10^{18}, and $4.0\times10^{17}\,\mathrm{cm}^{-3}$, calculated widths of carrier depletion zones are 23, 34, and 42 nm, respectively. The tendency of the increase of the width is the same; a lower dopant concentration leads to a wider zone. The difference in the width between calculated depletion zones and observed precipitate free zone, however, is significant. The differences are 37, 41, and 53 nm, for dopant concentration 3.5×10^{18}, 1.0×10^{18}, and $4.0\times10^{17}\,\mathrm{cm}^{-3}$, respectively. The origin of this difference is explained if one notes that each As cluster also has a carrier depletion zone as a result of incorporation of charge carriers in the cluster. If As clusters are redistributed in such a way that their depletion zones do not overlap with the depletion zone of the *pn* junction as shown in Fig. 5, the width of the precipitate free zone becomes significantly wider than the depletion zone of the *pn* junction. The width of the depletion zone around an As cluster is given by the equation:[7]

$$V_0=\frac{-qN_D}{3\epsilon}\left(\frac{r_s^3}{r_0}+\frac{r_0^2}{2}-\frac{3r_s^2}{2}\right), \tag{1}$$

where V_0, q, N_D, and ϵ are the built-in potential, electron charge, dopant concentration, and permittivity of GaAs, respectively. The radii of the As cluster and depletion region are represented by r_0 and r_s, respectively. By using this equation, we have estimated the difference in the width between the precipitate free zone and depletion zone of the *pn* junction, which is equal to $2(r_s-r_0)$. By assuming r_0 being 10 nm and V_0 being 0.6 V which is nearly half the band gap

of GaAs at 750 °C, $2(r_s-r_0)$ is 26, 40, and 56 nm for the dopant concentrations 3.5×10^{18}, 1.0×10^{18}, and $4.0\times10^{17}\,\mathrm{cm}^{-3}$, respectively. If the accuracy of the average widths of precipitation free zones is taken into account, these calculated values are considered to be in fairly good agreement with observed ones. It is also noted that the value $2(r_s-r_0)$ is nearly unchanged with the cluster size r_0 according to Eq. (1) and, hence, the width of the precipitate free zone is expected to remain nearly constant with coarsening of As clusters as observed in Fig. 3.

Redistribution of As clusters at the *pn* junction which is illustrated by Fig. 5 indicates that the redistribution occurs in the most efficient way for maximizing the areas of carrier depletion zones, that is, the area of intrinsic semiconductor regions. This implies that redistribution of As clusters is driven by the tendency of reducing free carriers in the semiconductor matrix, that is, the tendency of lowering the electronic free energy; a semiconductor having conduction electrons or holes is in a higher electronic energy state than an intrinsic semiconductor. The redistribution of As clusters at the boundary of the doped and undoped two layer structure at the time when free carriers have started to appear in the doped layer also supports the above explanation for the origin of the formation of precipitate free zones. When a number density of As clusters is high and their depletion zones cover the entire area of the doped region in the early stage of coarsening, no driving force exists for redistribution of the clusters. As the number density of clusters decreases with increase of their average size, the doped layer starts to have free carriers and, then, causes redistribution of clusters. It should however, be pointed out that this driving force is very small. For example, if one As cluster with a radius of 10 nm exists in a semiconductor matrix doped with $1\times10^{18}\,\mathrm{cm}^{-3}$ Si, only about 100 electrons are transferred from the GaAs matrix to the As cluster according to Eq. (1). The number of As atoms in the cluster, on the other hand, is roughly 250 000. If V_0 is assumed as 0.6 V again, only the energy of 2.4×10^{-4} eV per atom is gained by the transfer of conduction electrons from the GaAs matrix to the As cluster. The reason for the occurrence of redistribution of As clusters in spite of such an extremely small driving force is the nature of the coarsening stage of precipitation. At the coarsening stage, the matrix crystal has already become nearly stoichiometric and all precipitate clusters are placed in the matrix under the exactly same condition except for their sizes. If, therefore, even a very small difference exists between two regions of the matrix crystal such as the presence or absence of free carriers, redistribution of precipitate clusters will occur; the rate of redistribution, of course, should depend on the magnitude of the driving force caused by this difference.

In summary, the present observation of redistribution of As clusters at the *pn* junctions has shown that the redistribution is caused by the electronic state of the GaAs matrix, that is, the presence or absence of free carriers. This implies that the observed phenomenon is driven by a highly novel mechanism. There are a number of phase transitions which are directly influenced by electronic states of the systems, this case is one where the electronic state directly affect the process of precipitation. The results reported here also has another important implication. They provide solid evidence for the incorporation of both conduction electrons and holes by As clusters, implying that the clusters act as metallic particles in a semiconductor matrix. Because of the incorporation of both types of free carriers, As clusters are expected to act as efficient recombination centers of photoexcited electrons and holes which are suggested by an earlier study of the pump-prove experiments.[12]

ACKNOWLEDGMENT

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