Arsenic precipitates and the semi-insulating properties of GaAs buffer layers grown by low-temperature molecular beam epitaxy

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Arsenic precipitates have been observed in GaAs low-temperature buffer layers (LTBLs) used as "substrates" for normal molecular beam epitaxy growth. Transmission electron microscopy has shown the arsenic precipitates to be hexagonal phase single crystals. The precipitates are about 6 ± 4 nm in diameter with a density on the order of 10^{17} precipitates per cm^3. The semi-insulating properties of the LTBL can be explained in terms of these arsenic precipitates acting as "buried" Schottky barriers with overlapping spherical depletion regions. The implications of these results on LTBL resistivity stability with respect to doping and anneal temperature will be discussed as will the possible role of arsenic precipitates in semi-insulating liquid-encapsulated Czochralski-grown bulk GaAs.

Recently, a new type of semi-insulating GaAs epilayer, known as a low-temperature buffer layer (LTBL) was found to reduce "sidegating" or "backgating", an important parasitic problem associated with GaAs field-effect transistor circuit technology.[1] Even though there is currently much interest concerning possible applications of this material, there is a certain "mystery" about its chemistry, atomic structure, and electronic properties. Most of this mystery is well documented by Kaminska *et al.*[2] It can be summarized as follows. The LTBL is grown by molecular beam epitaxy (MBE) at about 200 °C using "standard" MBE parameters. Next, this LTBL is used as a "substrate" or "superstrate" upon which film structures for active GaAs devices, such as metal-semiconductor field-effect transistors (MESFETs) or high electron mobility transistors (HEMTs), are grown by MBE at "normal" substrate temperatures, i.e., in the vicinity of 600 °C. If the LTBL is characterized before continued growth or anneal at 600 °C, it has the following properties. At normal excitation intensities there is no measurable photoluminescence (PL) signal compared with that for "normal" buffer layers.[1] The LTBL has a >1 at. % excess arsenic over the stoichiometric amount and it is "highly resistive."[2] It has a "giant" electron paramagnetic resonance (EPR) signal corresponding to 5×10^{18} As antisites per cm^3 and it has a 0.1% larger lattice constant than for bulk GaAs.[2] However, if the LTBL is (1) "annealed" (defined as either a 600 °C, 10 min anneal or used for MBE growth at 600 °C) or (2) grown above 250 °C instead of at 200 °C and with or without a subsequent anneal, its properties change in a peculiar way. It is now found to have a very small PL signal with a decay time $\ll 100$ ps.[3] It still has a >1 at. % excess arsenic. It is now uniformly semi-insulating with a lattice constant the same as that for bulk GaAs, and it has no measurable EPR signal (resolution $\sim 10^{18}$ cm^{-3}). It has also been observed that LTBLs doped greater than 10^{18} Si atoms per cm^3 remain semi-insulating after a 600 °C anneal.[4,5]

Given that, to first order the above listed properties of the as-grown LTBL can be explained by the presence of a high concentration of antisite defects, there are at least two intriguing questions which come to mind concerning the annealed LTBL. First, how has the excess arsenic been redistributed? Second, what makes the annealed LTBL remain semi-insulating, especially highly Si-doped layers?

In this letter we show that for our growth conditions we observe the excess arsenic as hexagonal phase arsenic precipitates. Second, we show that the semi-insulating properties of the annealed LTBL can be explained by a simple model in which the arsenic precipitates act as buried Schottky barriers with "spherical" depletion regions. The layers become semi-insulating when either the doping level is low enough or the precipitate density is high enough for the depletion regions to overlap. Since Schottky barriers in GaAs have both large n-type (0.8 eV) and p-type (0.6 eV) barriers,[6] and thus deplete both donors and acceptors, our model can explain in simple terms why, for example, highly Si-doped annealed LTBLs are semi-insulating.[4,5]

The samples used in this work were grown in a Varian GEN II MBE system. The details of the film growth have been reported previously.[7] Transmission electron microscopy (TEM) images of cross-sectional specimens have shown the existence of a large number of small precipitates in the LTBL. These precipitates give rise to weak spots near spots of GaAs in electron diffraction patterns. By analysis of diffraction patterns and high-resolution electron microscope images, these precipitates have been identified as elemental arsenic having a hexagonal structure.[8] Figure 1 is a dark field image obtained by using one of the spots of

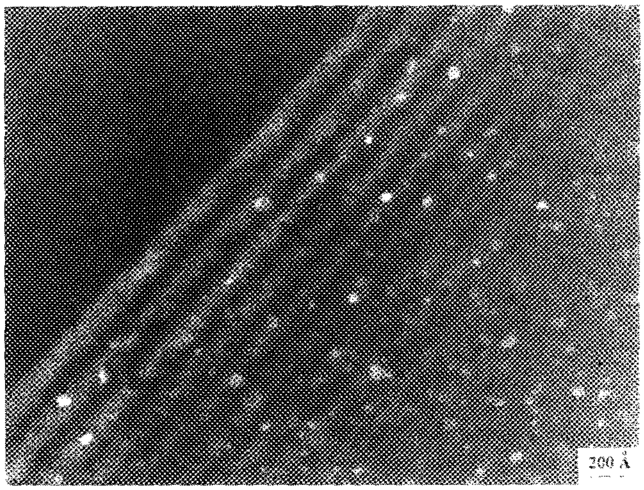

FIG. 1. Dark field image of the GaAs buffer layer grown at a substrate temperature of 220 °C. Arsenic precipitates are seen as bright sphere-like particles.

the arsenic precipitates. A weakly excited (111) spot of GaAs was also included in the objective lens aperture and, hence, gives rise to thickness contours. In the image, arsenic precipitates appear as bright sphere-like particles showing moiré fringes inside. Diameters of the arsenic precipitates range from 2 to 10 nm. Because of the nature of the dark field imaging technique, only a limited number of arsenic precipitates existing in the area can be seen in the observed image. Considering this effect, one can estimate that the density of arsenic precipitates in the LTBL is of the order of 10^{17}–10^{18} cm^{-3}. (This estimate was made by selecting sections of the TEM image where the sample thickness was approximately 1000 Å and counting the observed precipitates.) Using the lower limit of 10^{17} arsenic precipitates per cm^3 and a cluster radius of 3 nm, we estimate 5×10^{20} atoms of excess arsenic precipitates per cm^3 of GaAs which agrees well with the previously reported excess arsenic concentration of over 1 at. %, i.e., $>4\times10^{20}$ arsenic atoms per cm^3 of GaAs.[2] More details of the observation and analysis of the TEM images will be reported elsewhere.[9]

Given both the greatly decreased antisite defect concentration in annealed LTBLs and the existence of a high density of precipitates, it is tempting to recall the role of excess arsenic or arsenic clusters in the formation of Schottky barriers at metal/GaAs interfaces. Arsenic clusters can be associated with Schottky barrier formation either through their role in generation of metal-induced gap states (MIGs)[10] or in their role in native defect generation which pins the interface Fermi level at a value which corresponds to the Schottky barrier height.[11] Within this model, arsenic clusters will be surrounded by spherical depletion regions analogous to the planar regions at two-dimensional metal/GaAs interfaces, with characteristic barrier heights of $\phi_{bn}=0.8$ eV and $\phi_{bp}=0.6$ eV, for n- and p-type material respectively. When these depletion regions are isolated, namely for low cluster density, N_x, and/or high doping density, N_D, the GaAs will be partially compensated but still conducting as shown in Fig. 2(a). In

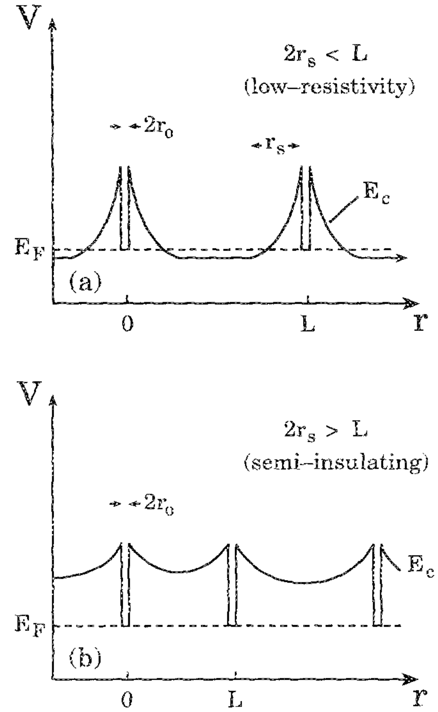

FIG. 2. Band bending for n-type semiconductor with isolated Schottky barrier clusters: (a) high doping/low cluster density, (b) low doping/high cluster density.

contrast, for high cluster density and/or low doping density the GaAs will be completely depleted and semi-insulating [Fig. 2(b)]. Solving Poisson's equation, it is found that the maximum depletion radius r_s is related to barrier height ϕ_b and cluster radius r_o by

$$\phi_b=(qN_D/6\epsilon)\,[(2r_s^3/r_o)+r_o^2-3r_s^2], \tag{1}$$

where N_D is the doping density. For a cluster radius of 3 nm, barrier height of 0.8 eV, and a doping level of 1×10^{18} cm^{-3}, the calculated depletion radius is about 190 Å so that depletion spheres will begin to overlap for cluster densities greater than 2×10^{16} cm^{-3}. A perhaps clearer explanation is obtained by calculating the amount of charge on a cluster. Laplace's equation gives

$$n_m=(4\pi\epsilon/q)\,r_o\phi_b, \tag{2}$$

where n_m is the number of electron charges. This number, times the cluster density, is the maximum density of dopants that the clusters can compensate, and for 3 nm clusters one obtains $n_-=22$ and $n_+=16$ for n- and p-type material, respectively. This model implies that for fixed cluster size, compensation limits are proportional to cluster density, as shown in Fig. 3. As can be seen, the cluster density in our LTBL will render GaAs semi-insulating for $N_D<2.2\times10^{18}$ cm^{-3} and $N_A<1.6\times10^{18}$ cm^{-3}. This value is in good agreement with previous n-type doping results in which the annealed LTBL is still semi-insulating for high Si-doping levels.[4,5] It should also be noted that in the crossover regime, where depletion spheres are starting to overlap but the GaAs is not yet completely depleted, conductivity will be affected by percolation behavior and will likely lead to hopping-like conductivity at low temperatures.

We should like to note that the nature of the arsenic

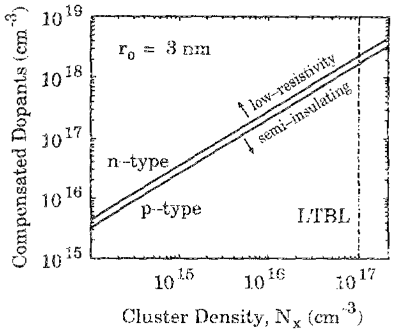

FIG. 3. Conductivity regime for n- and p-GaAs with 3 nm radius clusters. Upper left corresponds to Fig. 2(a) lower right to Fig. 2(b). The cluster density for the LTBL is indicated.

precipitation will very likely depend on both the thermochemical history of the LTBL and the kinetics associated with the transition from a supersaturated arsenic state to an equilibrium state when the LTBL is annealed. For example, Ref. 2 has no mention of arsenic precipitation. However, using samples similar to Ref. 2 arsenic precipitation has been reported recently.[12-14] Clearly, the excess arsenic concentration in the LTBL is determined by the MBE conditions, especially the As/Ga flux ratio and the substrate temperature during the low-temperature growth phase. The formation and properties of the arsenic precipitates must depend on the details of the anneal, especially anneal time, temperature, and strain environment. In this regard it is quite likely, for example, that a rapid thermal anneal (RTA) to high temperatures (750–900 °C) would cause some fraction of the arsenic precipitates to redissolve in the crystal lattice. This in turn would decrease the precipitate density and would result in highly doped LTBLs converting to low-resistivity material at least for one conductivity type. This effect has been seen in Si-doped LTBLs.[4]

We have recently used LTBL material as the photoconductor in an optoelectronic receiver for THz beams.[15,16] Due to the ultrafast turn-on of the photoconductivity of this material when driven with 70 fs laser pulses, 0.46 ps THz pulse widths were measured. Consequently, the bandwidth of the optoelectronic THz beam system[16] has been extended to beyond 2.5 THz for the first time. Since a photoexcited carrier must on average diffuse 10 nm to the nearest As precipitate, and since normal Schottky barrier contacts can capture both holes and electrons, we interpret our fast optoelectronic response as additional evidence that As precipitates act as buried Schottky barriers.

Finally, in Fig. 3 we extrapolate our results to lower arsenic precipitate densities for the purpose of speculating on the role arsenic precipitates play in rendering bulk liquid-encapsulated Czochralski (LEC) grown GaAs semi-insulating. This speculation is reasonable since deep level defects, i.e., EL2 and/or antisite arsenic defects, have been long correlated with arsenic-rich bulk crystal growth conditions.[17] Also, arsenic precipitates in bulk GaAs crystals have been previously reported.[18] Using Ref. 2 we find that the ratio of excess arsenic in LTBL GaAs to that in bulk LEC GaAs is about 100. In the spirit of speculative arguments we assume that this would correspond to LEC-grown material with an arsenic precipitate density which would be a factor of 0.01 for that of annealed LTBL or 10^{15} particles per cm^3. A more conservative argument would be that since the maximum EPR signal (5×10^{18} cm^{-3}) is approximately equal to 0.01 times the total excess arsenic concentration (5×10^{20} cm^{-3}) the total excess arsenic concentration in bulk LEC GaAs would be expected to be 100 times its EPR signal (10^{16} cm^{-3}). This would be 10^{18} arsenic atoms per cm^3 or 2×10^{14} precipitates per cm^3 assuming 6 nm diameter precipitates. Thus from Fig. 3 we see that for this mechanism, bulk GaAs doped less than mid 10^{15} cm^{-3} would be semi-insulating. This agrees qualitatively with the known carrier versus doping properties of LEC GaAs. (It can be shown that the compensation efficiency, namely the ratio of maximum compensation to excess arsenic, is proportional to $1/r_o^2$, so that conditions leading to small clusters will result in even greater compensation limits at the same density of excess arsenic.) The implications of this argument along with the experimental results of this study might lead to the following conjecture. Even though the arsenic antisite defect and the EL2 defect have been well studied and correlated, it is possible that they do not directly contribute to the semi-insulating character of the undoped GaAs found in technology applications. Rather, might it be possible that their signal is indicative of the presence of arsenic precipitates which in turn dominate the semi-insulating properties of undoped arsenic-rich GaAs? This notion might be a fruitful topic of further research.

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