Comment on "Mechanism responsible for the semi-insulating properties of low-temperature-growth GaAs" [Appl. Phys. Lett. 65, 3002 (1994)]

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In a recent letter in this journal, Liu *et al.*[1] drew a conclusion on the mechanism responsible for the semi-insulating properties of GaAs epilayers grown by molecular beam epitaxy (MBE) at low-substrate temperatures and subsequently annealed. They concluded that their experiments supported the "arsenic antisite defect" model[2] and not the "buried Schottky barrier" model.[3] We question some of their interpretations of the experimental data that led to this conclusion.

When GaAs is grown at low substrate temperatures by MBE with otherwise normal growth conditions, excess As is incorporated. These low-temperature-grown (LTG) GaAs epilayers are of high crystal quality[4] in spite of containing as much as 2% excess arsenic in the form of point defects.[5] With anneal this excess arsenic beings to precipitate.[6] The final composite structure of semimetallic arsenic precipitates in a GaAs matrix can be controlled with the substrate temperature during MBE and the subsequent anneal. The substrate temperature during MBE sets the amount of excess As in the epilayer;[7,8] the subsequent anneal controls the precipitation of the excess arsenic and the amount of coarsening of the arsenic precipitates.[9] Clearly, the properties of as-grown materials are controlled by point defects. However, there has been controversy concerning the role the arsenic precipitates play in the optical and electronic properties of the annealed LTG epilayers.

Liu *et al.*[1] used the technique of near-infrared absorption (NIRA) to determine the density of unionized arsenic antisites, As^0_{Ga}, in their epilayers as a function of anneal. However, to quantify the density of As^0_{Ga} in their epilayers, they assume the decrease in intensity of the infrared radiation is due *only* to absorption by the As^0_{Ga}. However arsenic precipitates have formed in their annealed epilayers and will play a role in the absorption and scattering of the infrared radiation.[10] Therefore Liu *et al.*[1] cannot assume that all the reduction in transmission of the infrared radiation is due to absorption by the As^0_{Ga}—for their 600 °C 30 min annealed sample, much of the reduction in radiation may actually be due to absorption and scattering by *the arsenic precipitates*.

Attributing the NIRA signal measured by Liu *et al.*[1] for their 600 °C 30 min annealed epilayer to absorption and scatter by the arsenic precipitates is lent credibility by comparing the Liu *et al.*[1] NIRA data with the Liu *et al.*[1] measurements of the ionized arsenic antisite density, As^+_{Ga}. Liu *et al.*[1] used magnetic circular dichroism of absorption (MCDA) to measure the As^+_{Ga} density. There is significant photoquenching of the MCDA signal seen in Liu *et al.*[1] Figure 2(c) for the sample that was annealed at 600 °C for 10 min. If any conclusions can be drawn from the MCDA signal displayed in Fig. 2(d) for the 600 °C 30 min annealed epilayer concerning the As^+_{Ga} concentration, then one can conclude photoquenching is occurring. Now looking at Fig. 1 of Liu *et al.*,[1] NIRA data are shown only for the as-grown epilayer and the epilayer that experienced at 600°C 30 min anneal. In the Fig. 1 NIRA data, significant photoquenching is observed for the as-grown sample but absolutely no photoquenching for the 600 °C 30 min annealed sample. Therefore different species must be giving rise to the MCDA signal, which is photoquenchable, and the NIRA signal, which is not photoquenchable—not just a difference in ionization state of the arsenic antisite. It is very likely the NIRA data in Fig. 1 for the 600 °C 30 min annealed epilayer is due to absorption and scattering by the arsenic precipitates.[10] [Compare Fig. 8 in Ref. 10 of the calculation of the absorption coefficient for a 1% volume fraction of arsenic precipitates in a GaAs matrix with Liu *et al.*[1] Fig. 1(b).]

Even if Liu *et al.*[1] could conclude that the Fermi level position is determined by the arsenic antisite in their epilayers, they are only looking at a subset of the material that is referred to as LTG-GaAs in the literature. The highest temperature anneal performed by Liu *et al.*[1] was 600 °C and the longest duration at this temperature was 30 min. Although not a light anneal, much higher temperature anneals are common—in the range of 700–1000 °C.[9] No definite conclusions can be made about these materials produced by higher temperature anneals based on the experiments of Liu *et al.*[1] However, the data in Fig. 3 of Liu *et al.*[1] display a decrease in the neutral and ionized arsenic antisite concentration with increase of anneal temperature. Extrapolating these data to higher temperature anneals would suggest a further decrease in concentration and the role of the arsenic antisites and hence an increase in the role of the arsenic precipitates. Also the actual arsenic antisite concentration could be significantly lower than displayed in Fig. 3, especially for the 600 °C anneals, since absorption or scattering of the infrared radiation by the arsenic precipitates was ignored in analyzing the NIRA data.

The conductivity as a function of a wide range of anneal temperatures for LTG-GaAs has been reported by Ibbetson *et al.*[11] They found that the room-temperature conductivity of a LTG-GaAs sample annealed for 30 s at 600 °C was due to hopping conduction. For higher temperature anneals, the room-temperature conductivity was not caused by hopping conduction but was due to a thermally assisted tunnelling process with an activation energy of ~0.6 eV, which they attribute to the arsenic precipitates. The results of Ibbetson

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et al.[11] lend credence to a transition occurring in annealed LTG materials as the excess arsenic precipitates and to a pinning position for the arsenic precipitates of ~0.6 eV below the conduction band. Using scanning tunneling microscopy (STM), Feenstra *et al*. have shown that in *n*-LTG-GaAs the arsenic precipitates produce midgap pinning and depletion spheres were observed around them.[12] Liu *et al.*[1] argues that because the Fermi level is near midgap in undoped LTG-GaAs as the precipitates form, little charge transfer is expected between the GaAs matrix and the arsenic precipitates. Clearly the amount of charge transfer will depend on the pinning position and concentration of the arsenic precipitates; and the concentrations of the arsenic antisites and gallium vacancies. If the pinning position of the arsenic precipitate is above the level of the arsenic antisite, then arsenic precipitates will be ionized and will be compensating gallium vacancies. If the arsenic precipitate pinning position and the arsenic antisite level are approximately at the same energy level, then they will play equal roles in compensating gallium vacancies. If the pinning position of the arsenic precipitates is below the arsenic antisite level, then the antisites will compensate the gallium vacancies; however, depending on the concentration of the arsenic antisites and the gallium vacancies, some of the arsenic precipitates may be negatively or positively charged. It should be noted that the conductivity measurements of Ibbetson *et al*.,[11] the STM measurements of Feenstra *et al.*,[12] and the photoreflectance measurements of Warren *et al.*[13] place the pinning position of the arsenic precipitates between $E_v+0.65$ eV and $E_v+0.8$ eV.

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