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Shifted x-ray photoelectron peak in molecular beam epitaxial GaAs grown at 200 °C

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X-ray photoelectron spectroscopic results show that molecular beam epitaxial GaAs grown at 200 °C has a reduced effective surface potential energy, about 0.5 eV, compared with the usual 0.7 eV. A Poisson analysis of the data, using parameters from Hall effect and absorption measurements, requires that the Fermi-level-controlling defect in this material must have a significantly lower activation energy than that of EL2, an unexpected result.

Molecular beam epitaxial (MBE) GaAs is typically grown at substrate temperatures of 580–600 °C in order to produce layers with low (<10¹⁴ cm⁻³) concentrations of impurity donors and acceptors and even lower concentrations (<10¹⁷ cm⁻³) of deep impurity and defect traps. However, it has recently been shown that MBE material grown at much lower temperatures, near 200 °C (called LTMBE GaAs), has very unique properties and can lead to new and improved devices. The outstanding feature of the 200 °C material is a highly As-rich nonstoichiometry which is manifested by dense (~10²¹ cm⁻³) As antisites (Asₐₐ) and As interstitials (possibly dimers), and after an anneal at 550–600 °C, As precipitates. We have reported another interesting and useful phenomenon, namely, that a thin layer (≥20 Å) of LTMBE GaAs grown on an n-type conductive GaAs layer reduces the free-carrier depletion in the conductive layer; equivalently, the band bending in the conductive layer must be lower than the usual 0.7 eV associated with the oxidized GaAs surface. As will be shown below, a realistic representation of the conduction band energy as a function of depth Eₐ(z) is as illustrated in Fig. 1. Here a 350 Å, 200 °C “cap” is grown on top of a conductive layer having a net shallow donor concentration Nₐ=2.4×10¹⁷ cm⁻³. With no cap, a region of thickness wₐ is depleted of free carriers, and with the cap, the depleted thickness is reduced to wₐ. Because the cap itself has negligible conductance, the values of wₐ and wₐ in Fig. 1 can be determined from Hall-effect measurements and, in fact, illustrate an actual case. Although the exact values of the donor concentration (Nₐ) and acceptor concentration (Nₐ) in the cap are not known (because the small cap thickness precludes accurate absorption measurements which can determine these quantities), it is clear from Hall-effect measurements that Eₐ must be flat over part of the cap, as shown. The reason is that wₐ remains constant as the cap is etched off, until only about 100 Å of the cap remains, at which point the surface and interface depletion regions in the cap are evidently starting to overlap. Essentially, a flatband (neutral) region in the cap isolates, or screens, the cap surface states from the conductive layer.

To determine Nₐ and Nₐ in 200 °C material we have used a thicker sample (2 μm) grown directly on a semi-insulating (SI) substrate, so that accurate absorption and Hall-effect measurements could be performed. The absorption analysis, which assumes that Nₐ=[Aₐₐ] and Nₐ=[Aₐₐ]⁺, gives Nₐ=9.9×10¹⁹ cm⁻³ and Nₐ=7.9×10¹⁸ cm⁻³, and the Hall-effect determination of Nₐ is very close to the absorption value. Although the absorption determination of Nₐ is somewhat inaccurate, it is within the range of values measured by electron paramagnetic resonance (EPR) on other samples grown in the same MBE system; thus, we have used these values of Nₐ and Nₐ in Fig. 1(b). Fortunately, the flat portion of Eₐ(z) in the cap does not depend critically on Nₐ and Nₐ but is more strongly influenced by Eₐ, the donor energy. To get the proper value of wₐ, as determined by Hall-effect measurements, it is necessary to set Eₐ=0.42 eV, as well be discussed later. Finally, we have followed a consensus in the literature by including a high surface acceptor density (1×10¹³ cm⁻²) at Eₐ=0.70 eV. Note that although such surface states are well verified in nor-

![FIG. 1. Conduction band diagrams for (a) an active layer alone, and (b) an active layer with a 350 Å cap grown at 200 °C. In both cases a surface acceptor density of 1×10¹³ cm⁻² at Eₐ=0.70 eV is assumed. The parameters wₐ and wₐ are effective depletion lengths.](image-url)
The samples for XPS analysis were grown in a Varian Gen II MBE apparatus on SI GaAs substrates. Each sample had a 500 Å undoped buffer layer, grown at 580 °C, and a 2500 Å, Si-doped active layer, with $n = 2.4 \times 10^{17}$ cm$^{-3}$, also grown at 580 °C. In addition, the “capped” sample contained a 1000 Å, undoped layer grown at 200 °C with As$_4$, while the uncapped simply had the normal, air-exposed surface. The capped sample was representative of many others grown under the same conditions. Note that a 1000 Å cap with the same $N_{As}$, $N_{As}$, and $E_{Dx}$ as the 350 Å cap in Fig. 1 differs only in the length of the flat $E_{C}$ region. However, the Poisson analysis converges more quickly for the thinner cap.

The XPS data were taken on a Surface Science Instruments M-Probe operating with a monochromatic AlK$_\alpha$ line at $E_{x}$ = 1486.6 eV. The instrument measures the kinetic energy $E_{k}$ of the emitted photoelectrons, and since $E_{k} = E_{x} - E_{\phi}$ (the spectrometer work function), it is easy to get $E_{\phi}$, the binding energy with respect to the Fermi energy. In Fig. 2, we schematically show an $n$-type semiconductor, in equilibrium with an XPS apparatus, for two different cases of semiconductor band bending. For case 2 the band bending is smaller, which means the binding energy ($E_{F} - E_{core}$) at the surface is larger. Thus, if the surface is passivated (smaller band bending), then $E_{\phi}$ will be larger. For samples which are not strongly conducting, the apparent energies can be shifted due to charging effects. To minimize this problem, we have used a neutralizing screen in front of the samples and out of focus with the analyzer. To further correct for charging effects, all As and Ga lines in a particular sample were referenced to the carbon 1s line (evidently surface carbon) in that sample. In Fig. 3 are presented the As 3d spectra for the control sample (no cap), and the 200 °C capped sample. Clearly, the capped sample spectrum is shifted to a higher binding energy (lower band bending). The spectra were fitted with Gaussian functions, after removing an integral (Shirley) background, in two different ways—assuming (1) that each line was a singlet, or (2) a spin-orbit-split doublet. The singlet fits were (assuming the C 1s line is at 285.00 eV): $E_{m} = 41.29$ eV and FWHM = 1.38 eV for the uncapped sample; and $E_{m} = 41.47$ eV and FWHM = 1.46 eV for the capped sample. Here $E_{m}$ is the energy at the spectral maximum and FWHM is the full width at half-maximum. The $E_{m}$'s in the raw data shown in Fig. 3 differ slightly from the above values because the C 1s lines actually appeared at 285.12 and 285.11 eV for the uncapped and capped cases, respectively. Also, over repeated runs on different samples the C 1s FWHM varied from about 1.43–1.48 eV, which provides an estimate of the probable error in the FWHM determinations.

To model the XPS data in our case is somewhat more complicated than usual, because as seen in Fig. 1 the conduction band $E_{C}(z)$ for the capped case varies appreciably ($\sim 0.11$ eV) over the effective electron emission depth $z_{0}$ (about 15 Å). Thus, the emitted electrons from each small element $d\Delta z$ about $z$ will contribute a Gaussian line shape centered at $E_{b}(z) = E_{b}(\infty) - [E_{C}(z) - E_{C}(\infty)]$ (see Fig. 2) and having a FWHM = $\Gamma$. Also, each of these Gaussians must be weighted by the probability of electron emission, $\exp(-z/z_{0})$. It is more convenient for display purposes to develop the analysis around $E_{C}(z) = E_{b}(\infty) + E_{C}(\infty) - E_{b}(z)$; then the normalized line shape $F(E)$ will be given by

$$F(E) = \frac{\int_{0}^{\infty} e^{-2.7707z} e^{-z/z_{0}} dz}{\int_{0}^{\infty} e^{-2.7707z} e^{-z/z_{0}} dz} e^{-2.7707z} e^{-z/z_{0}} dz,$$  

(1)

where $E_{m}$ must be found from the integral equation

$$E_{m} = \frac{\int_{0}^{\infty} E_{C}(z) e^{-2.7707z} e^{-z/z_{0}} dz}{\int_{0}^{\infty} e^{-2.7707z} e^{-z/z_{0}} dz} e^{-2.7707z} e^{-z/z_{0}} dz.$$  

(2)

(Note that $2.7707/\Gamma^{2} = 1/2\sigma^{2}$, the usual form of a Gaussian function, where $\sigma$ is the standard deviation.) For our XPS conditions, we can estimate $z_{0} = 15$ Å, and since $E_{C}(z)$ varies slowly for the uncapped sample, we can assume that $\Gamma = \Gamma$ (uncapped) = 1.38 eV. The results of applying this analysis to the Poison solutions of Fig. 1 are shown in Fig. 4. The $E_{m}$'s from Fig. 2 turn out to be 0.72 and 0.45 eV for the capped and uncapped samples respectively, and the linewidths are both close to the elemental width, $\Gamma = 1.38$ eV. It is interesting that the much larger initial (within $\sim z_{0}$) variation of $E_{C}(z)$ for the capped sam
The important new conclusion of this XPS/Hall/absorption study is that the deep donor which controls the Fermi level in the 200 °C cap material must be significantly shallower than EL2, which is known to have its first donor transition close to $E_C - 0.65$ eV at 296 K. Thus, the neutral (flatband) $E_F$ in the cap is 0.38 eV (see Fig. 1), which according to the Poisson fit arises from a donor level at $E_{DC} = 0.42$ eV (296 K). Although this value of $E_{DC}$ could be varied a few hundredths of an eV (by different choices of $N_{DC}$ and $N_{AOD}$, for example) and still be consistent with the Hall and XPS constraints, it could not be raised to 0.65 eV without violating both of these constraints. For example, $\omega_p$, which is determined by the Hall-effect experiment, depends only on the difference between the flatband energies in the cap and active layer as long as $N_{AOD} > N_{DC}$, and this latter condition must be true to satisfy the EPR and absorption experiments (i.e., $N_{AOD} > 10^{18}$ cm$^{-3}$). For $N_{AOD} > 10^{18}$ cm$^{-3}$, and $N_{DC} = 10^{20}$ cm$^{-3}$, known from absorption measurements, $E_{DC}$ cannot be very different from 0.42 eV and still give a flatband $E_F = E_{DC} - 0.38$ eV in the cap. In fact, such a near equality of the dominant defect or impurity level and the Fermi level is not unusual and indeed is what is nearly always found in semiconductor material.

In summary, XPS, Hall, absorption, and EPR measurements are all consistent with the values of $N_{DC}$, $N_{AOD}$, and $E_{DC}$ given in this letter. However, the value of $E_{DC}$ approximately 0.42 eV at 296 K, is significantly shallower than the value of 0.65 eV expected for EL2, and therefore the defect at $E_F - 0.42$ eV is not FI.2, although it may be related to the prime component of EL2, i.e., $A_{SO}$. The defect may also be related to $A_S$. In this regard, it should be pointed out that recent photo-EPR data have suggested that the dominant $A_{SO}$-related center in 200 °C GaAs has an activation energy less than that of EL2, although an actual value could not be assigned from those data.

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2F. W. Smith, in Ref. 1, p. 3.