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Mechanisms for GaAs surface passivation by a molecular beam epitaxial cap layer grown at 200 °C

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A thin, undoped, molecular beam epitaxial (MBE) GaAs cap layer grown on top of an n -type conductive layer significantly reduces the free-electron depletion from the latter. By analyzing electron transfer to surface, interface, and bulk acceptor states in the cap, as a function of cap thickness, we show that either (1) the usual $E_C-0.7$ eV surface states are absent, (2) a dense donor near $E_C-0.4$ eV exists or (3) a high donor interface charge ($\sim 5 \times 10^{12}$ cm $^{-2}$) is present. Any of these conclusions constitutes an important new aspect of low-temperature MBE GaAs.

INTRODUCTION

The Fermi energy E_{F_S} at the surface of almost all air exposed or metal covered n -type GaAs is known to be pinned at $E_{F_S} = E_C - 0.7$ eV.¹⁻⁶ This pinning, variously attributed to dense, defect acceptor states,⁴ unavoidable free-As coverage,⁶ or other causes, has a large, adverse effect on GaAs device development, especially with regard to metal-semiconductor and metal-insulator-semiconductor technologies;⁷ thus, much effort has been directed toward its understanding and elimination. The most successful surface treatments, so far, have included photochemical oxidation⁸ and applications of sulfur-bearing compounds, such as Na₂S and (NH₄)₂S.^{9,10} While these treatments have all greatly reduced the effective density of surface recombination centers, as evidenced by higher photoluminescence (PL) intensities, there is strong evidence that they have not reduced the density of surface acceptors, which pin E_{F_S} in n -type material.¹¹⁻¹³ Furthermore, none of the observed effects is stable for long times or at high temperatures. Recently, we have shown¹⁴ that a 100 Å layer of molecular beam epitaxial (MBE) GaAs grown at 200 °C on top of a normal conductive layer (grown at 580 °C) greatly reduces the usual free-carrier transfer from the conductive layer to surface states. This effect was interpreted as resulting from a reduced effective surface potential energy $-e\phi_s$. However, a 100 Å cap layer is too thick to be simply treated as a surface, and not only has the possibility of its own surface states, but also interface states, and bulk donor and acceptor states. All of these states must be considered in clarifying the mechanism of passivation. In the present study, we use 1000 Å caps to accentuate the bulk effects in the cap and facilitate etching experiments. The sheet Hall concentration n^{sh} is monitored as the cap thickness d_c is changed by etching. Clearly, from the results shown in Fig. 1, 200 and 400 °C caps exhibit much different behavior as d_c is changed.

THEORY

Free-carrier depletion in an n -type active layer¹⁵⁻¹⁷ occurs because of electron transfer to various groups of ac-

ceptor states: sheet interface acceptor states $N_{A_i}^{\text{sh}}$, at $z = 1000$ Å in Fig. 2; sheet surface acceptor states $N_{A_s}^{\text{sh}}$, at $z=0$; and bulk acceptor states N_{A_c} in the cap, $z=0$ to 1000 Å. We will first assume that the donors in the cap (of density N_{D_c}) are not significantly ionized, i.e., that these donor states lie well below E_F . Then, charge conservation requires that

$$N_{D_c}w = N_{A_i}^{\text{sh}-} + N_{A_c}d_c + N_{A_s}^{\text{sh}-} = f_i N_{A_i}^{\text{sh}} + N_{A_c}d_c + f_s N_{A_s}^{\text{sh}}, \quad (1)$$

where the left-hand (right-hand) side represents the positive (negative) charge. Here w is the thickness of the depletion region in the active layer next to the cap, and f_i and f_s are the negatively charged fractions of $N_{A_i}^{\text{sh}}$ and $N_{A_s}^{\text{sh}}$, respectively. Also, we have assumed that the bulk acceptors in the cap are below midgap so that $N_{A_c}^- = N_{A_c}$. The value of f_i is given by

$$f_i = \frac{1}{1 + g \exp\{-[E_i - (-e\phi_i)]/kT\}}, \quad (2)$$

where E_i is the absolute energy of the interface acceptors with respect to the conduction band, and the degeneracy factor g is the ratio of the unoccupied-state degeneracy to the occupied-state degeneracy. A similar equation holds for f_s . Note that if the interface species are donors, instead of acceptors, then the $f_i N_{A_i}^{\text{sh}}$ term in Eq. (1) is replaced by $-(1-f_i) N_{D_i}^{\text{sh}}$.

The sheet Hall concentration n^{sh} is very simply related to $N_{D_c}w$. According to Ref. 17,

$$\begin{aligned} n^{\text{sh}} &= \int_0^\infty n dz = N_{D_c}(d-w-w_1) = C - N_{D_c}w \\ &= C - (f_i N_{A_i}^{\text{sh}} + N_{A_c}d_c + f_s N_{A_s}^{\text{sh}}), \end{aligned} \quad (3)$$

where d is the total thickness of the active layer, w_1 is the thickness of the active-layer depletion region next to the buffer (not shown in Fig. 2), and C is a constant, known for our growth conditions but not critical anyway. We have assumed that the Hall r factor is unity, which is nearly

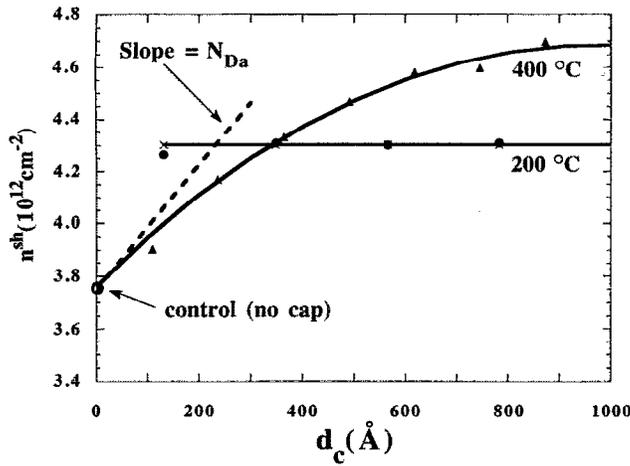


FIG. 1. The sheet free-electron concentration as a function of cap thickness.

correct for concentrations around $2 \times 10^{17} \text{ cm}^{-3}$ (actually, $r \approx 1.02$). In the work described here we vary d_c , which will in general affect f_i and f_s .

In Fig. 1, we show plots of n^{sh} vs d_c for three samples grown with a Varian GEN-II MBE system on the same day and under identical conditions, except for the cap growth. After growth, d_c was reduced in controlled steps by using a 1:1:40 $\text{H}_3\text{PO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$ etch. The 5000 Å, undoped buffer layers, and the 2500 Å, $2.4 \times 10^{17} \text{ cm}^{-3}$ Si-doped layers, were all grown at 580 °C and the two caps were grown at 200 °C and 400 °C, respectively. Several other samples grown at different times and in two different MBE systems have exhibited qualitatively identical behavior to those shown in Fig. 1, irrespective of whether d_c was varied by growth or etching. Also, a sample with a 580 °C cap had the same n^{sh} as one grown at 400 °C. Thus, 200 °C GaAs is clearly unique in that $dn^{\text{sh}}/d(d_c) \approx 0$.

To explain these phenomena, we differentiate Eq. (3)

$$\frac{dn^{\text{sh}}}{d(d_c)} = \frac{f_s^2(1-f_s)(N_{A_s}^{\text{sh}})^2 \lambda_T - N_{A_c}}{1 + w \lambda_T \{ f_s(1-f_s) N_{A_s}^{\text{sh}}(1+d_c/w) + f_i(1-f_i) N_{A_i}^{\text{sh}} [1 + f_s(1-f_s) N_{A_s}^{\text{sh}} d_c \lambda_T] \}}, \quad (5)$$

where $\lambda_T \equiv e^2/\epsilon kT = 549 \text{ \AA}$ at 296 K, and $w = (C - n^{\text{sh}})/N_{D_a}$, from Eq. (3). For the control sample, $w \approx 631 \text{ \AA}$, so that w , d_c , and λ_T are of similar magnitude except when the cap is nearly etched off ($d_c \rightarrow 0$). For donor interface states, $N_{A_i}^{\text{sh}}$ in Eq. (5) is simply replaced by $N_{D_i}^{\text{sh}}$ and Eq. (1) is modified as discussed earlier. Again, Eq. (5) holds only if the N_{D_c} are neutral or of negligible density.

DISCUSSION

We first apply this analysis to a cap layer of "normal" GaAs—that grown at 400 °C. By iteratively applying Eq.

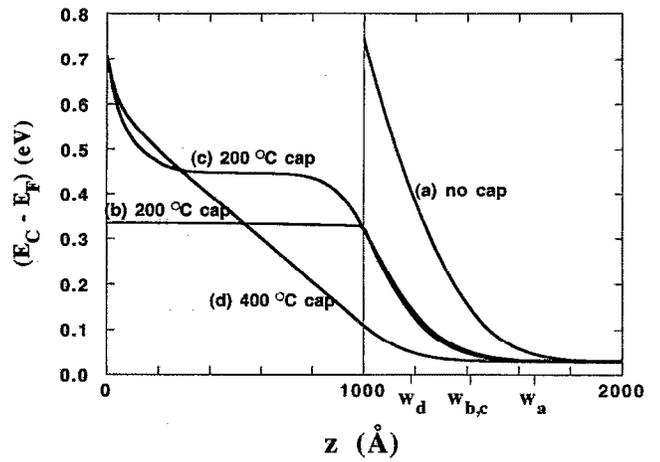


FIG. 2. The conduction band energy with respect to the Fermi energy as a function of depth for various cap parameters.

with respect to d_c after finding the d_c dependence of ϕ_s and ϕ_i from a depletion-approximation solution of the one-dimensional Poisson equation. For example, we determine ϕ_s from

$$\begin{aligned} -\phi_a + \phi_s &= -\frac{e}{\epsilon} \left\{ \int_0^{d_c} -z N_{A_c} dz \right. \\ &\quad \left. + \int_{d_c}^{d_c+w} z [-f_i N_{A_i}^{\text{sh}} \delta(z-d_c) + N_{D_a}] dz \right\} \\ &= -\frac{e}{\epsilon} \left\{ -N_{A_c} \frac{d_c^2}{2} - f_i(d_c) N_{A_i}^{\text{sh}} d_c + N_{D_a} \frac{w^2}{2} \right. \\ &\quad \left. + N_{D_a} w d_c \right\}, \quad (4) \end{aligned}$$

where ϕ_a is the flat-band potential, which begins at $z=d_c + w$ in the depletion approximation. The final result is

(5), consistent with the constraint given by Eq. (3), we get an excellent fit to the 400 °C data (Fig. 1) with the following parameters: $f_i=1$ (interface states below E_F) and $N_{A_i} = 1 \times 10^{11} \text{ cm}^{-2}$. This result is very understandable, because we would expect a larger surface charge ($f_s N_{A_s}^{\text{sh}}$) as we bring the surface states closer to the active layer. However, the 200 °C capped sample has $dn^{\text{sh}}/d(d_c) = 0$, which can occur over a large range of d_c only if both terms in the numerator vanish, within measurement error. If $f_s \neq 0$ or 1, then the solution requires $N_{A_s}^{\text{sh}} \approx 0$ and $N_{A_c} \approx 0$. The charge transfer to a 200 °C cap is then only to

the interface states N_{A_i} , which must equal $9.5 \times 10^{11} \text{ cm}^{-2}$ to produce the observed depletion in the active layer. Note that if $f_s = 0$ or 1, then even if there are surface states, there is no surface E_F pinning by them.

The exact Poisson equation solutions of $-e\phi(z) = E_C - E_F$ are plotted in Fig. 2. The depletion loss is equal to $N_{D_a} w_i$, where $i = a, b, c$, or d . A surface state acceptor concentration of $1 \times 10^{13} \text{ cm}^{-2}$ at $E_C - 0.7 \text{ eV}$ was assumed for the control sample [curve (a)] and the 400 °C capped sample [curve (d)], in order to pin the surface E_F close to that energy. The input parameters $N_{A_i}^{\text{sh}}$ were taken from the fits to Eq. (5) as given above. Here we have included a dense ($3 \times 10^{19} \text{ cm}^{-3}$), deep (0.65 eV at 296 K), EL2-like donor, known to exist from previous studies.¹⁸ This donor begins to influence $-e\phi$ only near 0.6 eV and causes some band bending there. However, the important point is that $-e\phi_s$ is "pinned" near 0.7 eV for both the 400 °C capped sample and the control sample. On the other hand, $-e\phi_s$ is not pinned at all for the 200 °C capped sample, but is represented by curve (b), nearly equal to the interface potential $-e\phi_b$, which, in turn, is determined by interface acceptor states. Such states could be formed from impurities impinging and sticking on the sample surface during cool-down from 580 to 200 °C, a problem also known to exist in growth interrupted samples.¹⁹

Because there is strong evidence²⁰ that $N_{A_c} \neq 0$, and in fact is $\approx 10^{18} \text{ cm}^{-3}$, we now consider a second possibility to explain the etching of the 200 °C capped sample. Note that curve (c) in Fig. 2 has nearly the same band bending in the active layer as has curve (b), the solution without surface states. Thus, the Hall measurements *before etch* cannot distinguish between the two cases, because the region depleted of free carriers (w_b or w_c) is nearly the same. To get curve (c), we assumed that besides the deep, 0.65 eV donor of concentration $3 \times 10^{19} \text{ cm}^{-3}$, the cap also had a shallower donor N_{D_2} at 0.46 eV, of concentration $2 \times 10^{18} \text{ cm}^{-3}$, and an acceptor N_{A_c} of concentration $1 \times 10^{18} \text{ cm}^{-3}$. We also assumed a surface state acceptor density of $1 \times 10^{13} \text{ cm}^{-2}$ at $E_C - 0.7 \text{ eV}$, as for curves (a) and (d). It is apparent by inspection that if we were to etch back the cap corresponding to curve (c), n^{sh} would remain constant until the flat-band region was gone, i.e., until the surface depletion region and the interface depletion regions in the cap began to overlap. From a depletion-approximation point of view, curve (c) is easy to analyze:

$$w_{c0} = \left[\frac{2\epsilon(-\phi_c + \phi_a - kT/e)}{eN_{D_a}(1 + N_{D_a}/N_{A_c})} \right]^{1/2} = 435 \text{ \AA}, \quad (6)$$

where ϕ_c and ϕ_a are the flat-band potentials (both negative numbers) in the cap and active layer, respectively. Since w_{c0} is always known from experiment, a given value of N_{A_c} determines a value for $\phi_c = -E_{F_c}/e$. Also, E_{F_c} is related to N_{D_c} and E_{D_c} through the expression

$$E_{F_c} = E_{D_c} - kT \ln \left[g \left(\frac{N_{D_c}}{N_{A_c}} - 1 \right) \right], \quad (7)$$

where g was defined earlier. The reported values of N_{D_c} range from 1×10^{19} to 1×10^{20} , and those of N_{A_c} , 1×10^{18} to $1 \times 10^{19} \text{ cm}^{-3}$. Inserting these values, along with a range of g from 0.5 to 2.0, into Eqs. (6) and (7) gives a possible spread of E_{D_c} from 0.3 to 0.5 eV below the conduction band edge. Obviously, such a donor is significantly shallower than the known 296 K As_{Ga} level, which is $E_C - 0.65 \text{ eV}$.

To get the measured w_c without the shallower donor, it is necessary to invoke an interface donor concentration $N_{D_i}^{\text{sh}}$. Again, a straightforward depletion-approximation solution of the Poisson equation can be cast in the form

$$N_{D_i}^{\text{sh}} = N_{D_a} w_c \{ [1 + (1 + N_{A_c}/N_{D_a})(w_{c0}^2/w_c^2 - 1)]^{1/2} - 1 \}, \quad (8)$$

where w_{c0} is the value of w_c if $N_{D_i}^{\text{sh}} = 0$, as given by Eq. (6). By assuming $E_{D_c} = 0.65 \text{ eV}$ and $g = 2$ ($\text{As}_{\text{Ga}}^{0/+}$ transition) and typical reported values $N_{D_c} = 1 \times 10^{20} \text{ cm}^{-3}$ and $N_{A_c} = 1 \times 10^{19} \text{ cm}^{-3}$, we get $E_{F_c} \approx 0.58 \text{ eV}$ from Eq. (7) and $w_{c0} = 562 \text{ \AA}$ from Eq. (6). Then, to get the experimental value $w_c = 406 \text{ \AA}$ requires $N_{D_i}^{\text{sh}} \approx 5.2 \times 10^{12} \text{ cm}^{-2}$, from Eq. (8).

SUMMARY

To summarize, a 400 °C cap (or a 580 °C cap) is well characterized by a small concentration of N_{A_c} ($\approx 10^{15} \text{ cm}^{-3}$) but a large concentration of surface acceptor states $N_{\text{As}}^{\text{sh}}$ which pin E_F near $E_C - 0.7 \text{ eV}$. A 200 °C cap, on the other hand can be possibly characterized in three different ways: (1) small N_{A_c} and small $N_{\text{As}}^{\text{sh}}$; (2) large N_{A_c} ($\approx 10^{18} \text{ cm}^{-3}$) and even larger N_{D_c} at $E_C - 0.3$ to 0.5 eV; or (3) large N_{A_c} and larger N_{D_c} at $E_C - 0.65 \text{ eV}$ (As_{Ga}), but also with a high interface donor concentration, $N_{A_i}^{\text{sh}} \approx 5 \times 10^{12} \text{ cm}^{-2}$. In the latter two cases, $N_{\text{As}}^{\text{sh}}$ cannot be determined from the Hall-effect measurements, since the surface states are screened from the active layer by a neutral region in the cap. Case (1) seems to be inconsistent with EPR results,²⁰ which suggest $N_{A_c} \approx 10^{18} \text{ cm}^{-3}$, although there are no measurements of N_{A_c} in very thin (1000 Å) layers. Recent x-ray photoelectron data, to be discussed elsewhere, suggest that the average potential in the top 10–20 Å is close to $E_C - 0.5 \text{ eV}$, rather than the usual $E_C - 0.7 \text{ eV}$. This result would be inconsistent with case (1), and possibly with case (3), but more studies are necessary for a complete understanding of the 200 °C material.

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- ¹J. Bardeen, *Phys. Rev.* **71**, 717 (1947).
- ²V. L. Rideout, *Solid State Electron.* **18**, 541 (1975).
- ³H. Shen, M. Dutta, L. Fotiadis, P. G. Newman, R. P. Moerkirk, W. H. Chang, and R. N. Sacks, *Appl. Phys. Lett.* **57**, 2118 (1990).
- ⁴W. E. Spicer, I. Lindau, P. R. Skeath, C. Y. Su, and P. W. Chye, *Phys. Rev. Lett.* **44**, 420 (1980).
- ⁵P. Masri, *Phys. Rev. Lett.* **64**, 208 (1990).
- ⁶J. L. Freeouf and J. M. Woodall, *Appl. Phys. Lett.* **39**, 727 (1981).
- ⁷F. Heliodore, M. Lefebvre, G. Salmer, and O. L. El-Sayed, *IEEE Trans. Electron Devices* **ED-35**, 824 (1988).
- ⁸S. D. Offsey, J. M. Woodall, A. C. Warren, P. H. Kirchner, T. L. Chappeli, and G. D. Petit, *Appl. Phys. Lett.* **51**, 33 (1987).
- ⁹E. Yablonovitch, C. J. Sandroff, R. Bhat, and T. Gmitter, *Appl. Lett.* **51**, 439 (1987).
- ¹⁰R. S. Besser and C. E. Helms, *J. Appl. Phys.* **65**, 4306 (1989).
- ¹¹E. Yablonovitch, B. J. Skromme, R. Bhat, J. P. Harbison, and T. J. Gmitter, *Appl. Phys. Lett.* **54**, 555 (1989).
- ¹²T. Sawada, H. Hasegawa, and H. Ohno, *Jpn. J. Appl. Phys.* **26**, L1871 (1987).
- ¹³C. J. Spindt and W. E. Spicer, *Appl. Phys. Lett.* **55**, 1653 (1989).
- ¹⁴D. C. Look, C. E. Stutz, and K. R. Evans, *Appl. Phys. Lett.* **57**, 2570 (1990).
- ¹⁵A. Chandra, C. E. C. Wood, D. W. Woodard, and L. F. Eastman, *Solid State Electron.* **22**, 645 (1979).
- ¹⁶T. R. Lepkowski, R. Y. DeJule, N. C. Tien, M. H. Kim, and G. E. Stillman, *J. Appl. Phys.* **61**, 4808 (1987).
- ¹⁷D. C. Look, C. E. Stutz, and K. R. Evans, *Appl. Phys. Lett.* **56**, 668 (1990).
- ¹⁸D. C. Look, D. C. Walters, M. O. Manasreh, J. R. Sizelove, C. E. Stutz, and K. R. Evans, *Phys. Rev. B* **42**, 3578 (1990).
- ¹⁹K. Tappura, A. Salokatve, K. Rakennas, H. Asonen, and M. Pessa, *Appl. Phys. Lett.* **57**, 2313 (1990).
- ²⁰M. Kaminska, Z. Liliental-Weber, E. R. Weber, T. George, J. B. Kortright, F. W. Smith, B-Y. Tsaur, and A. R. Calawa, *Appl. Phys. Lett.* **54**, 1881 (1989).