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Electron energy barriers at interfaces of GaAs(100) with $LaAlO_3$ and Gd_2O_3

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Electron energy barriers at the interfaces of GaAs(100) with Gd_2O_3 appear to be insensitive to the Fermi level pinning indicating that charges at interface states are of marginal importance for the band alignment at semiconductor/insulator interfaces. The inferred conduction band offset of 1.6 ± 0.1 eV for GaAs(100)/Gd_2O_3 is close to that measured at the GaAs(100)/$LaAlO_3$ interface which is consistent with the 5.8 and 5.7 eV wide band gaps of these two insulators. However, the defects revealed by photoionization measurements exhibit a distinctly different in-depth distribution. In GaAs/$LaAlO_3$ most of the traps are located close to the semiconductor surface, while in GaAs/Gd_2O_3 case they are found distributed across the entire oxide layer. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2338893]

Based on recent successes achieved in the deposition of non-native oxide insulators bringing the possibility of realizing functional metal-insulator-semiconductor (MIS) devices on GaAs closer to reality, great attention is now focused on studies of GaAs/insulator interfaces.[1–3] This stimulates investigation of the physical and chemical mechanisms governing the energy distribution of electron states, both band and defect related, at the interfaces of GaAs with insulating oxides. In this letter we consider the possible influence of the semiconductor surface states on the interface energy barriers. Recent results indicate that charges present at the interface between a polycrystalline Si electrode and HfO_2 alter the electron energy barriers significantly.[4] Analysis of GaAs interfaces would allow us to clarify the physical picture of this barrier perturbation because the GaAs interface states basically represent the surface states of the semiconductor crystal, i.e., they are geometrically located close to the crystal surface plane. We found that the GaAs interfaces with high interface state density ($>10^{13}$ cm^{-2}) leading to a "pinned" (or quiescent[5]) Fermi level have a barrier for electrons close to that found at the interface in the case of an "unpinned" Fermi level (using the Ga_2O_3 surface passivating layer).[6] This result indicates that the impact of the surface state charges would be of minor significance and allows one to use the band offset values determined at the pinned interfaces in all other cases. In a broader physical perspective, this observation suggests that the controlled modification of the interface barrier would require charges located inside the insulator to ensure sufficient variation of electrostatic potential. This information may be of great benefit when applied to the metal-insulator interface to control the threshold voltage.

The studied samples were prepared on *n*-type GaAs(100) epitaxial layers ($n_d \approx 2\times10^{16}$ cm^{-3}) using molecular beam deposition of two rare-earth based oxide insulators. Polycrystalline Gd_2O_3 was deposited from effusive evaporation of Gd in an oxygen ambient[7] and amorphous $LaAlO_3$ using e-beam evaporation under vacuum pressure below 10^{-8} Torr.[8] In contrast to the previous studies in which a Ga_2O_3 passivating template was used,[6,7] 31–37 nm thick oxides were grown directly on the GaAs crystal surface. For the sake of comparison, polycrystalline Ga_2O_3 layers of 14–16 nm thick on GaAs(100) were also studied, as well as $LaAlO_3$ layers grown by molecular beam deposition on H-terminated Si(100).[9] In the latter case a low pressure of O_2 (5×10^{-6} Torr) was maintained which was found to improve the insulating properties of the oxide. Nevertheless, no detectable oxidation of Si was observed (with detection limit of 0.02 nm) indicating negligible impact of oxygen at this pressure on the composition of interface itself.[9] Next, MIS capacitors were formed by thermoresistive evaporation of semitransparent (13 nm thick) Au or Al electrodes onto the oxide, and used in internal photoemission (IPE) and photoconductivity (PC) measurements performed at room temperature over the photon energy range $h\nu=2-6.5$ eV with a constant spectral resolution of 2 nm.[10,11] The quantum yield (Y) was determined by normalizing the measured photocurrent to the incident photon flux. Supplemental capacitance-voltage and conductance-voltage measurements could not reveal any space charge effects suggesting that the Fermi level in GaAs is pinned at the interface with the investigated rare-earth oxides because of the high (at least 10^{13} cm^{-2}) density of interface states.

The IPE/PC yield is shown in Fig. 1 as measured in GaAs/Gd_2O_3 MIS structures with +2 V (open symbols) or −2 V (filled symbols) applied to Au (circles) or Al (squares) gate electrodes. The spectra reveal that the yield is remarkably insensitive to the orientation of electric field in the oxide and to the work function of the metal electrode. This observation suggests that the dominant contribution to the photocurrent flowing across the oxide film results from charge carriers generated in the bulk of the Gd_2O_3 layer, either due to band-to-band excitation (intrinsic PC) or due to photoionization of some gap states. The only asymmetry in the currents measured under different bias polarities is ob-

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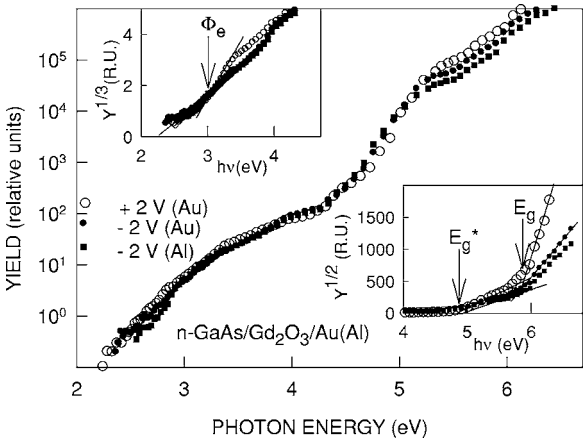

FIG. 1. IPE/PC yield as a function of photon energy in *n*-type GaAs(100)/Gd_2O_3 (32.5 nm) MIS capacitors measured under different voltages applied to Au (circles) or Al (squares) electrodes. The determination of the electron IPE threshold Φ_e and the oxide band gap width E_g from the $Y^{1/3}$-$h\nu$ and $Y^{1/2}$-$h\nu$ plots is illustrated in insets in the upper left and bottom right of the figure, respectively. The arrows indicate the resolved spectral thresholds.

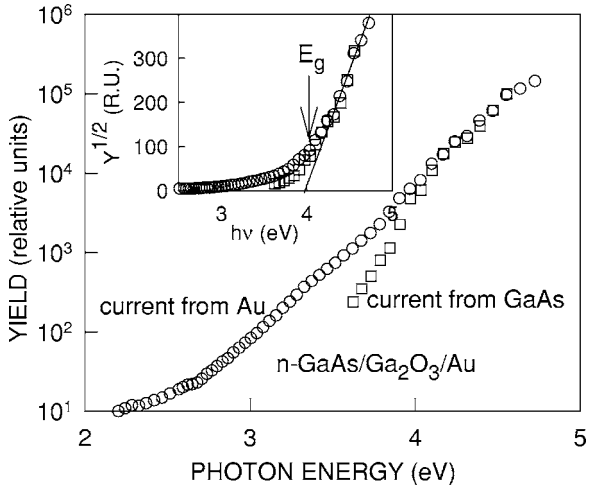

FIG. 2. PC yield as a function of photon energy measured in *n*-type GaAs(100)/Ga_2O_3 (16.2 nm)/Au MIS capacitors under voltages corresponding to different current flow directions. The determination of the oxide band gap width E_g using the $Y^{1/2}$-$h\nu$ plot is illustrated by the inset.

served in the photon energy range $3<h\nu<4$ eV in which a slightly enhanced current under positive bias indicates a contribution of electron IPE from GaAs to the photocurrent. This spectral portion is exemplified (see top left inset in Fig. 1) in $Y^{1/3}$-$h\nu$ coordinates which enable the determination of the energy barrier for photoemission from the semiconductor valence band (Φ_e),[12,13] i.e., between the top of the GaAs valence band (VB) and the bottom of the oxide conduction band (CB) in our structures. The Φ_e values derived from the spectra measured at different positive bias voltages (not shown) depend only weakly on the strength of electric field in the oxide and yield the zero-field barrier height of 3.1 ± 0.1 eV. This value is close to the barrier evaluated earlier for the Gd_2O_3 subnetwork in $GdGaO_x$ insulators grown on top of the passivating Ga_2O_3 template.[6] Thus, the Fermi level pinning does not lead to any measurable barrier height variation. This agreement is also important from the affirmative point of view because the strong field dependence of the IPE spectral threshold caused by the Ga_2O_3 interlayer (cf. Fig. 4 in Ref. 6) suggests a considerable built-in electric field which might also affect the zero-field barrier height. As it appears now, the latter effect is not dramatic and the barrier between the GaAs VB and the Gd_2O_3 CB is close to 3 eV yielding the CB offset of 1.6 ± 0.1 eV at the GaAs(100)/Gd_2O_3 interface.

The intrinsic PC of Gd_2O_3 also appears to be similar to the behavior of $GdGaO_x$ (Ref. 6) with the major PC threshold at 5.8 ± 0.1 eV corresponding to the oxide band gap E_g as shown in the bottom right inset in Fig. 1. As indicated, we also observed a subthreshold "tail" with apparent onset at $E_g^*=4.8\pm0.1$ eV apparently related to the polycrystalline structure of the Gd_2O_3 film. Worth of reminding here is that an enhancement of this tail is observed with increasing Ga content in $GdGaO_x$.[6] The observation of a similar subthreshold PC in pure Gd_2O_3 suggests that the tail states are likely caused by irregular bonding configurations of Gd cations. Apparently then, the enhancement of PC at $h\nu>4.8$ eV with increasing Ga concentration in $GdGaO_x$ layers may be explained either by the upshift of the Ga-related unoccupied states when the Ga cation subnetwork is diluted in the more wide gap Gd_2O_3 matrix,[14] or else by the perturbing action of Ga ions on the neighboring Gd cations. The PC threshold of pure Ga_2O_3 films determined from the data shown in Fig. 2 appears to be considerably lower: $E_g(Ga_2O_3)=4.0\pm0.1$ eV (cf. inset in Fig. 2). As a final note, in the low-energy portion of the Gd_2O_3 spectra shown in Fig. 1 ($h\nu<3$ eV) the dominant contribution to the current stems from defects with photoionization threshold $E_t=2.5-2.7$ eV, which are also observed in $GdGaO_x$.[6]

The results of the IPE/PC experiments on GaAs/$LaAlO_3$ samples are summarized in Fig. 3. The figure also shows the data for the (100)Si/$LaAlO_3$(20 nm) interface (squares) with an unpinned Fermi level. Comparison of the PC spectra [cf. ○ and □ in Fig. 3(b)] indicates that the intrinsic PC of amorphous $LaAlO_3$ has close spectral thresholds in the layers deposited both on GaAs and Si. This suggests good reproducibility of the oxide electronic structure in these films with a band gap width of 5.7–5.8 eV and ≈1 eV subthreshold excitation tail, consistent with previous reports.[6,14,15] However, in the low photon energy range [$h\nu<3.5$ eV in Fig. 3(a)] significant differences between the two semiconductor crystals are observed from the measurements under positive metal bias (open symbols). In the case of Si, a clear onset of electron IPE from the semiconductor VB is observed at $h\nu=3.1$ eV [cf. □ in Fig. 3(a) and in the inset in Fig. 3(b)], while the GaAs sample (○) exhibits a tail-like spectrum stretching to low photon energies which is inconsistent with sharp VB edge in semiconductors. Rather, this kind of spectrum points to photoionization of imperfections in the insulating layer distributed over a wide energy range. Only under higher bias the GaAs/$LaAlO_3$ interface starts to show (cf. △ and ▽ in Fig. 3) a feature which can be associated with electron IPE from the GaAs VB into the oxide CB, as schematically shown in the inset in Fig. 3(a). The corresponding spectral thresholds determined from $Y^{1/3}$-$h\nu$ plot [inset in Fig. 3(b)] lie in the range of 2.8–2.9 eV and, when extrapolated in the Schottky coordinates to zero field (not shown), yield a barrier height $\Phi_e=2.9\pm0.1$ eV, corresponding to a CB offset of 1.5 ± 0.1 eV. Worth of noticing here is that the subthreshold photocurrent is much more intense in the case of GaAs than in the case of Si (cf. △ and □ in Fig. 3 corre-

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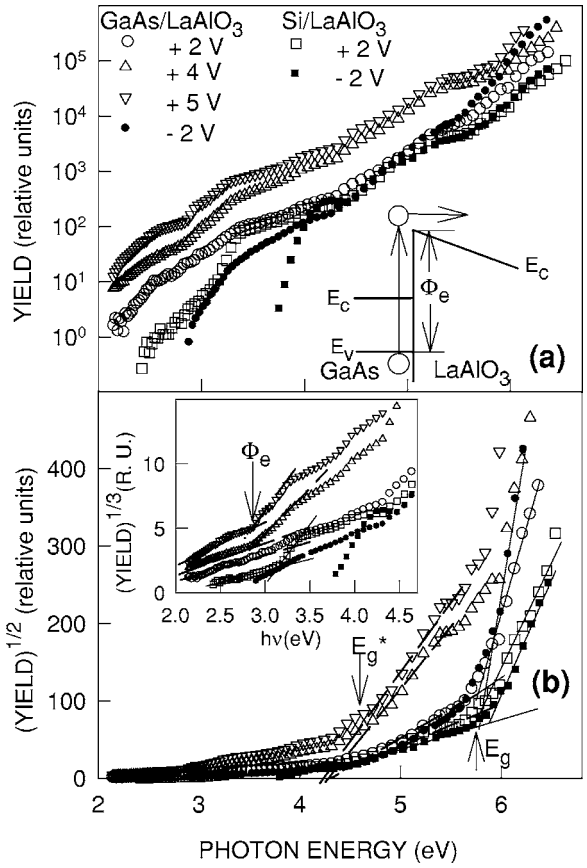

FIG. 3. (a) IPE/PC yield as a function of photon energy measured in *n*-type GaAs(100)/$LaAlO_3$ (37 nm)/Au capacitors for different voltages on the metal electrode (circles and triangles), compared to the Si(100)/$LaAlO_3$ (20 nm)/Au structure (squares). The determination of the band gap width from the $Y^{1/2}$-$h\nu$ plot and the electron IPE threshold Φ_e shown in the inset in panel (a) from the $Y^{1/3}$-$h\nu$ plot are illustrated in panel (b) and included inset, respectively. The arrows indicate the resolved spectral thresholds.

sponding to close average strengths of the electric field in the oxide). The most likely explanation of this behavior is optical excitation of GaAs/$LaAlO_3$ interface states distributed in energy above the semiconductor VB top.

It is found that the IPE/PC spectra of GaAs/$LaAlO_3$ MIS capacitors measured under negative metal bias (● in Fig. 3) show little sensitivity to the type of metallization (Au or Al, curves for Al not shown). The quantum yield in the spectral range $h\nu < 4.5$ eV appears to be comparable to the yield of hole IPE from Si into $LaAlO_3$ (■ in Fig. 3) despite the much lower density of states near the bottom of the CB in GaAs than in Si. Thus, we cannot correlate the corresponding transitions neither with electron IPE from states near the Fermi level of a metal (significantly different in Al and Au) nor with the IPE of holes from the semiconductor CB states. Most likely, the photocurrent in the spectral range $3 < h\nu < 4.5$ eV is caused by excitation of some defect states in $LaAlO_3$. The important feature here is the difference between the photocurrent spectra measured in GaAs/$LaAlO_3$ MIS structures under positive or negative bias. This indicates that optical excitation from imperfections does not occur uniformly across the oxide layer but rather at one of the interfaces, leading to the transport of different charge carriers at different bias polarities. Therefore, as the properties of the $LaAlO_3$/metal interface are expected to be similar for the Si and GaAs substrates, the results concerning $LaAlO_3$ grown on GaAs(100) and Si(100) suggest that in the former case a high density of imperfections is formed in the oxide region close to GaAs surface.

We may summarize the major results of the present study as follows. First, a high density of semiconductor surface states seems to have only a marginal effect on the interface band alignment as suggested by the close energy barriers observed at the GaAs/rare-earth oxide interfaces with pinned and unpinned Fermi levels. The interface dipoles appear to be insignificant and the derived CB offset of 1.5–1.6 eV represents the "intrinsic" value. Second, the type of semiconductor substrate may have a significant impact on the defect density occurring at the interface even if atomically controlled deposition is used as revealed by comparison of the interfaces of amorphous $LaAlO_3$ with GaAs and Si. Finally, Gd_2O_3 layers exhibit a high density of gap states in the bulk of the layer in the same energy range as in $GdGaO_x$ layers,[6] which may point to relationship of these traps to Gd cations. This observation suggests the possibility of intrinsic charge trapping in Gd_2O_3 insulators leading to device instability.

[1] A. Callegari, P. D. Hoh, D. A. Buchanan, and D. Lacey, Appl. Phys. Lett. **54**, 332 (1989).
[2] M. Passlack, M. Hong, and J. P. Mannaerts, Appl. Phys. Lett. **68**, 1099 (1996).
[3] M. Passlack, J. K. Abrokwah, R. Droopad, Z. Y. Yu, C. Overgaard, S. I. Yi, M. Hale, J. Sexton, and A. C. Kummel, IEEE Electron Device Lett. **23**, 508 (2002).
[4] V. V. Afanas'ev, A. Stesmans, L. Pantisano, and P. J. Chen, Appl. Phys. Lett. **86**, 072107 (2005).
[5] J. G. Swanson, Microelectron. Eng. **22**, 111 (1993).
[6] V. V. Afanas'ev, A. Stesmans, M. Passlack, and N. Medendorp, Appl. Phys. Lett. **85**, 597 (2004).
[7] M. Passlack, N. Medendorp, R. Gregory, and D. Braddock, Appl. Phys. Lett. **83**, 5262 (2003).
[8] B.-E. Parka and H. Ishiwara, Appl. Phys. Lett. **82**, 1197 (2003).
[9] L. F. Edge, D. G. Schlom, J. R. Williams, S. A. Chambers, C. Hinkle, G. Lucovsky, Y. Yang, S. Stemmer, M. Copel, B. Höllander, and J. Schubert, Appl. Phys. Lett. **84**, 4629 (2004).
[10] V. K. Adamchuk and V. V. Afanas'ev, Prog. Surf. Sci. **41**, 111 (1992).
[11] V. V. Afanas'ev, A. Stesmans, and M. O. Andersson, Phys. Rev. B **54**, 10820 (1996).
[12] R. J. Powell, J. Appl. Phys. **41**, 2424 (1970).
[13] J. M. Ballantyne, Phys. Rev. B **6**, 1436 (1972).
[14] V. V. Afanas'ev, A. Stesmans, C. Zhao, M. Caymax, T. Heeg, J. Schubert, Y. Jia, D. G. Schlom, and G. Lucovsky, Appl. Phys. Lett. **85**, 5917 (2004).
[15] V. V. Afanas'ev, A. Stesmans, L. F. Edge, D. G. Schlom, T. Heeg, and J. Schubert, Appl. Phys. Lett. **88**, 032104 (2006).

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