Stability of a low-temperature grown GaAs surface layer following air exposure using tunneling microscopy

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The stability of a GaAs layer structure consisting of a thin (10 nm) layer of low-temperature-grown GaAs on a heavily n-doped GaAs layer, both grown by molecular beam epitaxy, has been studied using a scanning tunneling microscope. The sample was exposed to the atmosphere between the layer growth and STM characterization. Tunneling spectroscopy shows both the GaAs band edges and a band of midgap states associated with the excess As in the surface layer. The observation of midgap states following atmospheric exposure indicates that the low-temperature-grown GaAs layer does not oxidize rapidly. The spectroscopy results are used to confirm a model for conduction in low resistance, nonalloyed contacts employing comparable layer structures. © *1996 American Institute of Physics.* [S0003-6951(96)01716-8]

Low-temperature grown (LTG) GaAs, i.e., layers grown by molecular beam epitaxy (MBE) at substrate temperatures of 250-300 °C, has been shown to possess a number of interesting electronic properties associated with the excess arsenic concentration incorporated during growth.[1] In as-grown LTG:GaAs material, the excess arsenic results in a large concentration (1×10^{20} cm^{-3}) of point defects, due primarily to arsenic antisite defects.[2,3] The pinning of the Fermi level near midgap in this material is generally associated with the point defects.

Recently, *ex situ* low-resistance, nonalloyed contacts to n- and p-type GaAs have been demonstrated using a structure consisting of a thin layer of LTG:GaAs (2-5 nm) on a highly doped layer of normal growth temperature GaAs, both grown by MBE.[4] In this study, specific contact resistances as low as $2\times10^{-7}\Omega\bullet$ cm^2 have been reported on n-type GaAs layers. The conduction model for the contact structure consisted of defect assisted tunneling through the LTG:GaAs layer and tunneling through the space charge region in the heavily doped layer. It was postulated that the LTG:GaAs layer did not significantly oxidize during prolonged exposure to the atmosphere.[4] In order to evaluate the suitability of the contact structure for device applications, it is important to determine the stability of the surface layer following air exposure.

As evidence for the instability of most GaAs surfaces, previous STM spectroscopy studies on GaAs surfaces have required special preparation procedures to avoid surface oxidation and the associated loss of STM resolution. Cleaved (110) surfaces have been prepared by either *in situ* cleaving in an ultra high vacuum (UHV) STM system or *ex situ* cleaving followed by sulfide passivation.[1–3,5] GaAs(001) surfaces passivated with As cap layers have been studied in UHV STM experiments following removal of the As layer by heating in the STM vacuum system.[6] STM spectroscopy has been performed on an unannealed layer of LTG:GaAs (225 °C) capped with a layer of GaAs grown at 350 °C. Characterization of a (110) surface of the LTG:GaAs layer exposed by cleaving in UHV identified a band of midgap states associated with the excess arsenic.[1–3] For heavily doped n-type (n+) layers, this band of states was located above the valence band edge of the material.

In order to characterize the stability of LTG:GaAs after air exposure, STM spectroscopy studies were performed on a layer structure comparable to the nonalloyed contact layers discussed above. While the STM measurements were performed under UHV, the sample was exposed to the atmosphere for a period of approximately 20 minutes during transfer from the MBE system to the STM chamber. After initial measurements were made, the sample was stored in a nitrogen filled desiccator for ~25 hours to further study the effect of ambient on the mid-gap states in LTG:GaAs. The observation of a band gap, along with a band of midgap states above the valence band edge, confirms that the LTG:GaAs surface layer does not significantly oxidize during atmospheric exposure and confirms the defect-assisted tunneling model for the contact structure.

The layer structure shown in Fig. 1 was grown in a Varian Gen II MBE on an epi-ready n$^+$ GaAs(100) substrate. The doped layers were grown at the typical GaAs growth temperature of 580 °C. The top (undoped) layer was grown at 250 °C in order to incorporate excess arsenic. The growth rate was 1 μm/hour. A silicon filament was used to dope the layers n-type. This allows doping concentrations of at least an order of magnitude higher than possible with conventional effusion cells.

It has been shown that the surface Fermi level is pinned near midgap during MBE growth of GaAs.[7] As a conse-

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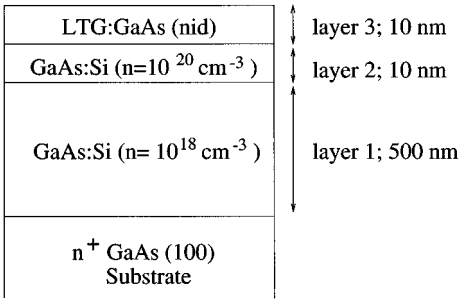

FIG. 1. A schematic diagram of the GaAs structure investigated. The characterization of the 10 nm thick LTG:GaAs layer (layer 3) after exposure to ambient is of particular interest.

quence, Si dopant atoms located within the surface carrier depletion region are incorporated primarily at donor sites, even for Si doping concentrations approaching the solid solubility limit. The presence of a LTG:GaAs cap layer maintains the high space charge density near the top of the heavily doped layer and therefore maintains the high concentration of activated donors within the region.

The wafer was unloaded and transferred in a vacuum package (P=50 millitorr) to the UHV STM apparatus so that it was exposed to air for the shortest possible amount of time. During transfer, the wafer was exposed to atmosphere for approximately 20 minutes.

The UHV STM used to characterize the LTG:GaAs layer is a homebuilt system with a computer controlled digital feedback system, as described elsewhere.[8,9] The base pressure of the stainless steel vacuum chamber is below 4×10^{-10} Torr. The tips are etched Pt/Ir wires cleaned in the STM chamber by field emission prior to use.

To investigate the uniformity of the LTG:GaAs layer, a few special procedures were developed. Initially, large scale scans (~300 nm in extent) of the LTG:GaAs surface were taken in order to search for localized non-uniformities. None were observed. In order to obtain I(V) data at many locations, a scanning routine was developed that periodically halted a normal topographic scan to obtain I(V) data. Using this procedure, following the completion of a typical topographic scan, an array of 10×10 I(V) curves were obtained. The results presented here are from a typical topographic scan covering a 50×70 nm range. It follows that the set of 100 I(V) scans obtained were approximately separated from each other by a 5×7 nm lateral offset. By simultaneously acquiring an STM topograph, a reliable procedure was implemented to guard against possible tip crashes or tip switches while acquiring I(V) data. At each location, a predetermined number (usually 70) of I(V) curves were taken and averaged together to reduce noise. The averaged signal was used to recover the local density of states at that location by calculating dI/dV and I/V numerically from I(V).

In what follows, the density of states (DOS) is represented by

$$DOS \propto \frac{dI}{dV} \times \frac{V}{I} \ . \tag{1}$$

Dividing the differential conductivity dI/dV by I/V serves to remove the slowly varying transmission function inherent in

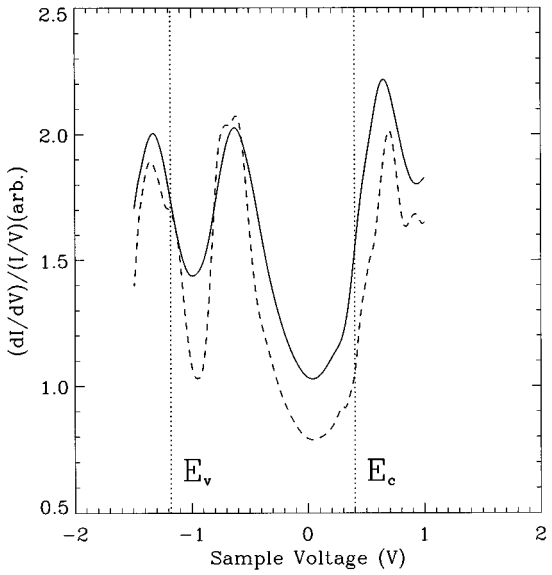

FIG. 2. Normalized conductance of LTG:GaAs as a function of sample voltage after 20 minutes exposure to ambient. The dashed line is a typical set of data obtained at an arbitrary location of the Pt/Ir tip. The solid line is the average of data obtained from 100 different spatial locations in 50 nm×70 nm area.

all I(V) data, resulting in a quantity that more closely mirrors the desired DOS. As suggested by Martensson and Feenstra, smoothing the conductance (I/V) to reduce DOS features provides a better approximation to the tunneling transmission function.[10] As discussed in Ref. 10, satisfactory results were obtained by smoothing the conductance with a one pole, low-pass Fourier filter algorithm with a pole frequency specified by δ^{-1}. By choosing δ larger than E_g, the semiconductor gap, the low-pass Fourier filter suppresses DOS features within the band gap. As a result, the transmission function (which should not depend on the gap structure) can be recovered to a better approximation. In this way, Feenstra *et al.* were able to recover reliable electronic spectra of GaAs containing arsenic-related point defects.[11] Since the bulk GaAs gap is $E_g=1.43$ eV, in this study the differential conductance (dI/dV) was normalized using the conductance (I/V) broadened by a low-pass Fourier filtering with a cutoff frequency of $1/\delta=1/1.6V^{-1}$.

Figure 2 shows the normalized conductance obtained after 20 minutes exposure to ambient air. The dashed line is a representative scan at a specific spatial location, while the solid line is the average of the scans at 100 spatial locations in 50×70 nm area. The effective conduction and valence band edges (marked by E_c and E_v), along with a band of gap states near the valence band edge are observed. In order to have a well-defined criterion for locating the band edges, the inflection point determined from the second derivative of I(V) was used to define an effective band edge. Although this procedure probably overestimates the size of the band-gap, it does provide a reliable way to compare band-gaps from I(V) data obtained at different locations. Following this procedure, the measured effective gap was found to be 1.58 eV in Fig. 2, a value slightly larger than the band gap of bulk GaAs (1.43 eV). From Fig. 2, the gap states are centered at a sample bias voltage near -0.64 V. Using the valence band

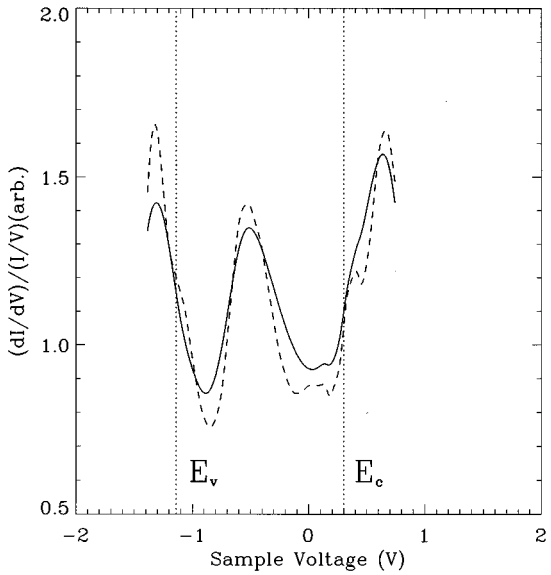

FIG. 3. Normalized conductance of LTG:GaAs as a function of sample voltage after 25 hours of storage in a nitrogen filled desiccator. The dashed line is a typical set of data obtained at an arbitrary location of the Pt/Ir tip. The solid line is the average of data obtained from 100 different spatial locations in 50 nm×70 nm area.

edge as a reference, this translates into a state located 0.54 eV above the effective valence band edge. The location of this feature is similar to the one observed in UHV-cleaved, n-doped LTG:GaAs.[2,3]

From the array of I(V) data, it is also possible to assess the integrity of the LTG:GaAs layer. In 88 of the 100 scans taken at different spatial locations, evidence for a clear gap state peak is found. In the other 12 scans, noisy data resembling the GaAs band gap was observed. The spatial distribution of midgap state density is consistent with the previous reports of defect densities in LTG:GaAs.[1–3]

During the course of the measurements described above, the sample was stored in the UHV chamber for a period of ~3 weeks. During this time, no significant degradation of the mid-gap states was detected. In order to further assess the stability of the mid-gap states in the LTG:GaAs layer, the sample was removed from the UHV chamber and stored in a nitrogen filled desiccator for 25 hours. Figure 3 shows the data obtained after reinserting the sample into the UHV STM chamber. The GaAs band edges as well as the gap states can be readily resolved without dramatic change. This data shows that the electronic properties of the structure are stable and convincingly supports the claim that LTG:GaAs does not rapidly oxidize upon exposure to air.

In summary, this study supports the claim of a reduced oxidation of LTG:GaAs when exposed to ambient conditions. This remarkable behavior was previously invoked to explain the ohmic contact experiments on a similar sample structure with a thinner ($\leqslant$5 nm) LTG:GaAs layer by Patkar *et al.*[4] A reduced contact resistance was observed and was explained by a defect-assisted tunneling mechanism through the LTG:GaAs. In the present study, we find that the normalized conductance shows an enhanced gap state, centered at 0.54 eV above the effective valence band edge. The location of this state is consistent with the results of Feenstra *et al.* obtained from a cleaved LTG:GaAs layer.[2,3] Data taken after 20 minutes exposure to ambient, after ~3 weeks in a UHV chamber, and after 25 hours storage in a nitrogen filled desiccator show no degradation of this gap state and suggest that reliable electrical contacts to buried GaAs-based heterostructures are now possible using this LTG:GaAs as a contact intermediate.

Note added in proof. Measurements using other techniques have confirmed the inhibited surface oxidation in comparable structures. We postulate that the inhibited surface oxidation can be attributed to the low concentration of minority carrier holes in the surface layer arising from the small minority carrier lifetime in the LTG:GaAs material.

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