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M. Kemerink,[a] J. W. Gerritsen,[b] P. M. Koenraad, H. van Kempen,[b] and J. H. Wolter
COBRA Inter-University Research Institute, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB, The Netherlands

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Spectrally resolved scanning tunneling microscope-induced luminescence has been obtained under ambient conditions, i.e., at room temperature, in air, by passivating the sample surface with sulfur. This passivation turned out to be essential to suppress the local anodic oxidation induced by the tunneling current. From the dependence of the luminescence signal on tunneling current and voltage, we find that the passivation solution and post-passivation annealing temperature strongly modify the surface density of states (SDOS). More specifically, we found evidence that, after annealing at 400 °C, no SDOS is left above the bottom of the conduction band. For annealing at 200 °C, the SDOS is found to be extended up to 1.0 ± 0.2 eV above the bottom of the conduction band. In all cases, the passivated (001) surface appears to be completely pinned. © *1999 American Institute of Physics.* [S0003-6951(99)01949-X]

The booming number of scanning probe techniques has enormously increased the potential for nanoscale experiments in the past decade. However, the complicated nature of many of these techniques has often prevented a wide spread usage. This holds specially for scanning tunneling microscope (STM)-induced luminescence (STL) on III/V semiconductors, being an ideal tool for studying structural and optical properties simultaneously.[1,2] The main problems encountered with STL on this material system are the extremely low count rates and surface oxidation. The former usually inhibits spectral resolution if practical integration times are required, while the latter often forces one to use an ultrahigh vacuum system.

A well-known solution of the surface oxide problem in ambient STM experiments is sulfur passivation.[3] The price to be paid is that one has to tunnel through a largely unknown surface density of states (SDOS), that depends on the sulfur solution in which the sample is dipped[4] and the temperature during the following, optional, annealing step.[5] Since the pinning of the Fermi level E_F at the surface depends on the surface DOS, this is also largely unknown.

No spectrally resolved STL measurements on III/Vs have been reported which were taken under ambient conditions using a reasonable, i.e., in the nA range, tunneling current. However, photon-mapping[6] and time-resolved[7] STL measurements on GaAs surfaces under, respectively, HV and ambient conditions were reported. Finally, Wenderoth, Gregor, and Ulbrich[8] demonstrated STL under ambient conditions, using a 1–2 nm thick gold layer to passivate the GaAs surface.

In this letter, we report on spectrally resolved STL on a sulfur passivated, single AlGaAs/InGaAs quantum well (QW) under ambient conditions. Moreover, we show that the integrated intensity versus tip-sample voltage curves can directly be related to the surface DOS, which is found to depend critically on the passivation procedure.

The active structure is grown by molecular-beam epitaxy on top of an undoped GaAs substrate and a short-period superlattice. It consists of a single 83 Å wide $In_{0.10}Ga_{0.90}As$ well layer, embedded between two 450 Å wide center Be-doped $Al_{0.25}Ga_{0.75}As$ barrier layers. The structure is capped by 170 Å undoped GaAs. The hole concentration in the well is $6\times10^{15}\,m^{-2}$. A Ni/Zn/Au contact was used as anode during STM experiments. From room temperature photoluminescence it is found that the well luminescence is situated around 920 nm. The sample has been characterized in detail in an earlier publication.[9]

We found that the unpassivated surface is rapidly etched away at the required biases due to local anodic oxidation (LAO).[10] Apart from giving rise to a highly unstable tunneling current, the LAO process also etches away the active layers within minutes when the scan mode is disabled. It is worthwhile to point out that we succeeded in observing an STL signal without passivating the surface by removing the native oxide with ammonia and immediately placing the sample in the STL setup. Probably this is due to the relatively slow growth rate of native oxide layers, after the first GaAs layer has been oxidized.[11] The sulfur passivated surfaces, on the other hand, are fully inert to LAO at all applied biases. Consequently, the tunneling current is also far more stable. Before passivation, the native oxide is removed by stirring the sample for 2 min in a 1:10 HCl (37%):H_2O solution. Afterwards, the sample is directly plunged into the passivation solution, which is either a supersaturated solution of Na_2S in iso-propanol (samples I, II, and III) or $(NH_4)_2S$ in H_2O (sample IV). After 2 min the sample is rinsed with de-ionized water and dried. Finally, samples II and III were annealed for 10 min at 200 and 400 °C, respectively.

STL experiments in *planar* configuration (see inset of Fig. 1) were performed under ambient conditions, using a home-built STM that has been described earlier.[12] Negative tip-sample biases V_t, ranging from -2 to -5 V, were applied with tunneling currents I_t up to 10 nA. From topology measurements, it was confirmed that no modification of the surface arose during tunneling. Nevertheless, the STL mea-

[a]Electronic mail: m.kemerink@phys.tue.nl
[b]Also at Research Institute for Materials, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

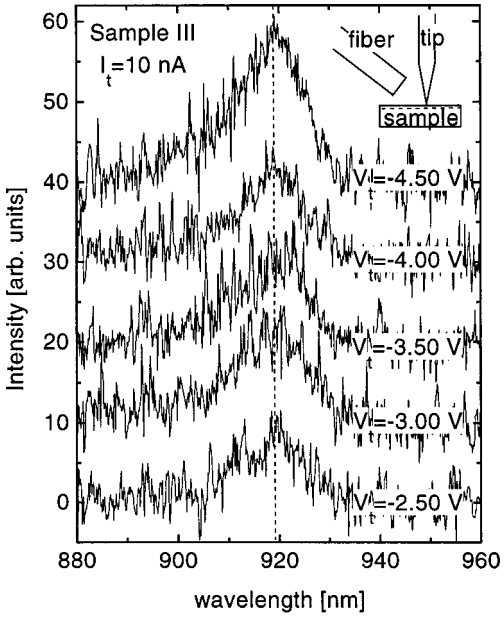

FIG. 1. STL signal from sample III at various V_t and $I_t = 10$ nA. The integration time is 10 min. The insert schematically depicts the setup which is operated in ambient.

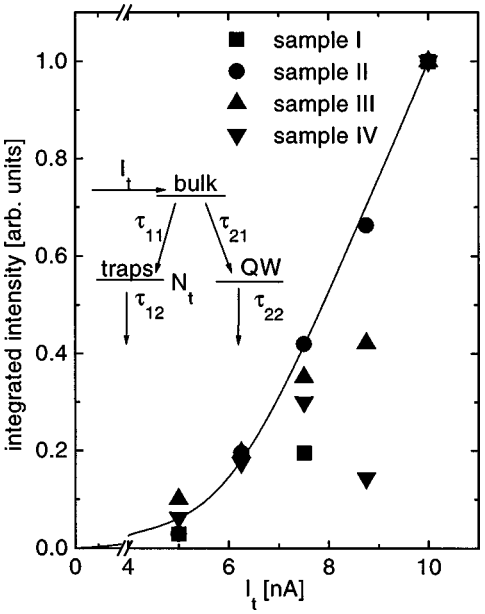

FIG. 2. Integrated STL intensity (normalized) vs I_t at $V_t = -3.5$ V. The line is calculated from a three-level rate-equation model. Insert: Illustration of the rate-equation model. N_t is the number of available traps, the t_{ij} are relaxation times.

surements were performed while scanning, and a new spot on the sample was used after each measurement. The emitted light was collected with a fiber bundle and analyzed with a 0.25 m monochromator in combination with a cooled Si charge coupled device camera. The typical separation between the fiber end and the tunneling contact was 1.5 ± 0.5 mm. With a total fiber area of 0.16 mm^2, this gives a detection angle of 0.09 ± 0.05 Sr.

The STM tips were electrochemically etched from 0.150 mm Pt wire. Etched tips were chosen to avoid the risk of loosing luminescence signal due to blocking of light by the bulk of the tip, which may well occur for thicker cut tips. The tips were prepared in a four-step process, as described by Libioulle *et al.*[13]

Figure 1 shows the STL signal from the InGaAs QW at various tip-sample biases. It should be noted that no luminescence from the GaAs layers was detected. From the integrated intensity we can deduce an effective electron-to-photon conversion efficiency of the order of 2×10^{-8}. Since this is several orders of magnitude lower than the estimated quantum efficiency of the QW, we conclude that the majority of the injected electrons is lost in nonradiative recombination channels. The absence of a Stark shift for all samples can either be interpreted in terms of a full pinning of E_F by surface states or in terms of screening by the topmost doping layer. The doping density in the top barrier is 1×10^{16} m^{-2}, which can, assuming a zero SDOS, maximally screen a tip-sample voltage of 0.5 V. From self-consistent envelope function calculations,[9] we estimate the Stark shift between the spectra at $V_t = -2.5$ V and $V_t = -4.5$ V to be of the order of 20 nm, in the absence of Fermi level pinning. Our data show that the Stark shift, if present at all, is maximally about 2 nm. This allows us to conclude that the pinning of E_F is, at least, almost complete for all samples studied. Similar results were found by Gwo *et al.* for the S-passivated GaAs(110) surface.[3]

The STL intensity of all samples is plotted versus I_t in Fig. 2. To facilitate comparison of samples, the intensities are normalized on the value at 10 nA. No significant differences in absolute intensity between the samples could be determined, because of the relatively large uncertainty in the solid detection angle. It is, however, clear from Fig. 2 that the intensity versus current curves are qualitatively the same for all samples. We interpret the apparent non-linearity in terms of saturation of a nonradiative recombination channel, which is illustrated in the insert of Fig. 2. For low current densities, all injected electrons are trapped in nonradiative recombination centers. At high enough currents, the traps saturate and electrons are able to reach the quantum well were they can recombine radiatively. The ionized Beryllium dopants are tentatively assigned as the nonradiative traps, which makes the areal trap density $n_t = 3 \times 10^{15}$ m^{-2}, i.e., half the 2D hole concentration since only the traps between the surface and the QW are to be taken into account. The line in Fig. 2 is a fit to the data based on this model, using for the time constants (as defined in the insert of Fig. 2) $\tau_{11} = \tau_{21} = 10^{-12}$ s, which we kept equal for simplicity, and $\tau_{12} = 2.5 \times 10^{-9}$ s; The time constant for radiative recombination from the well, τ_{22}, is not incorporated since we assume that the carrier capture of the QW does not depend on the occupation of carriers in the well. The current to the well, I_{21}, is therefore simply $I_{21} = eN_b/\tau_{21}$, with N_b the number of carriers in the bulk. The current to the traps, I_{11}, is $I_{11} = eN_b(1-f_t)N_t/\tau_{11}$, with f_t the occupancy of the available traps. The number of available traps N_t is taken as $N_t = \pi r^2 n_t$, with r the average radial distance the electrons travel before they are trapped by either the traps or the QW, which we fixed on a value of 100 nm.[14] Although the good agreement with the experimental data is apparent, the used parameter values should only be regarded as indicative of the order of magnitude. The reason is that the model is not sensitive to their absolute values, but only to their mutual ratios. However, it is important to note that the onset current, which

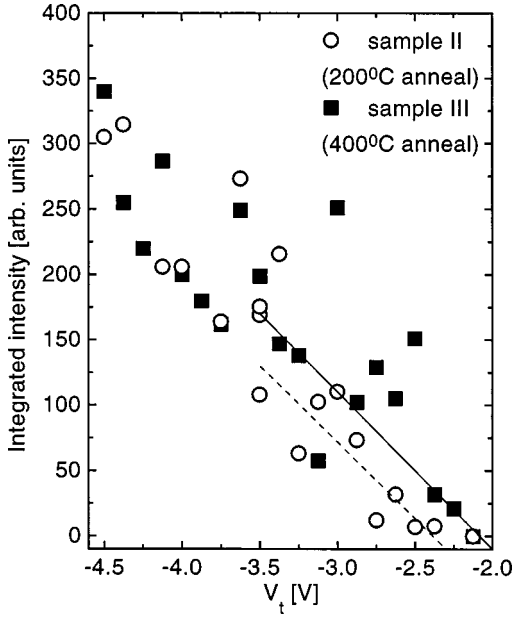

FIG. 3. Integrated STL intensity of samples II and III vs V_t. The lines guide the eye at low biases.

is basically $N_t t_{12}$ ($=6$ nA for the parameters used), is independent of the surface treatment. Therefore, we conclude that, after sulfur passivation, the main part of the nonradiative recombination centers is not located at the surface but in the bulk. This is in accordance with the assumption that the ionized Be atoms are the main trapping centers.

Significant differences between the samples annealed at 200 and 400 °C become visible when the integrated STL signal is plotted versus tip-sample bias (Fig. 3). Both samples show a linearly increasing intensity once the bias voltage exceeds an onset value. We estimate the onset value of V_t to be -2.4 ± 0.2 and -2.1 ± 0.2 V for samples II and III, respectively. This difference can be understood in terms of the surface density of states. It is known that after annealing at 360 °C or higher, the surface is covered by a monoatomic layer of S atoms that are bound to Ga atoms.[5] The corresponding SDOS was calculated in Ref. 5 and found to be extended from approximately 1.3 eV below to 0.5 eV above the top of the valence band. Electrons injected into the conduction band ($V_t<1.4$ V) are thus not hindered by these surface states. The onset voltage should therefore correspond to ballistic injection of electrons over the $Al_{0.25}Ga_{0.75}As$ barriers. Theoretically, this mechanism is expected to have its onset around -1.8 eV. Although in reasonable agreement, the present data do not unambiguously support this proposition.

When (part of) the sulfur atoms are As bound, which is the case for unannealed or low-temperature annealed surfaces, the SDOS is drastically different. The calculated SDOS of a S monolayer on an As-terminated surface[5] is extended from about 2.2 eV below the top of the valence band to 1.2 eV above the bottom of the conduction band. Electrons injected in this range are likely to be trapped and the STL signal will be weak or absent. From the onset voltage of luminescence, we estimate that the top of the SDOS lays 1.0 ± 0.2 eV above the bottom of the conduction band, in agreement with the theoretical result of Ref. 4.

Note that for biases larger than the onset value, a quadratic dependence of the integrated intensity versus bias is expected, due to the requirement of momentum conservation for electrons being injected over a barrier.[15] In the case of the Ga–S terminated surface, the relevant barrier is located at the GaAs–AlGaAs interface, whereas in case of the As–S terminated surface, the sample surface itself is the relevant barrier. However, the scatter in the data of Fig. 3 does not allow us do draw any firm conclusions concerning the power of the voltage dependence of the intensity. We do want to stress that the intensity differences between samples II and III at low biases are significant and have been reproduced on several spots on the same sample and on two sets of samples, prepared on different days.

In summary, we have shown that under ambient conditions, the STM can be used to induce luminescence from III/V semiconductors by passivating the sample surface with sulfur. Independent of the followed passivation procedure, the Fermi level is pinned by the surface density of states. In addition, we found evidence that annealing the passivated sample at 200 °C for 10 min leaves a surface that consists mainly of S atoms bound to As, which has a SDOS that is extended up to 1.0 ± 0.2 eV above the conduction band edge. Similarly, a 400 °C anneal appears to give rise to a strongly reduced SDOS, which is attributed to dominance of S–Ga bounds at the surface. We believe that these results can be of great interest for future research, in which optical properties of semiconductor nanostructures are investigated with nanometer resolution.

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