Luminescence Spectroscopy of Semiconductor Surfaces and Interfaces

L. J. Brillson
Xerox Webster Research Center, New York, brillson.1@osu.edu

S. Chang
Xerox Webster Research Center, New York

A. D. Raisanen
Xerox Webster Research Center, New York

I. M. Vitomirov
Xerox Webster Research Center, New York

Follow this and additional works at: https://digitalcommons.usu.edu/microscopy

Part of the Biology Commons

Recommended Citation
Available at: https://digitalcommons.usu.edu/microscopy/vol1995/iss9/14

This Article is brought to you for free and open access by the Western Dairy Center at DigitalCommons@USU. It has been accepted for inclusion in Scanning Microscopy by an authorized administrator of DigitalCommons@USU. For more information, please contact digitalcommons@usu.edu.
LUMINESCENCE SPECTROSCOPY OF SEMICONDUCTOR SURFACES AND INTERFACES

L.J. Brillson*, S. Chang, A.D. Raisanen and I. M. Vitomirov

Xerox Webster Research Center, 800 Phillips Rd 114/41D, Webster, NY 14580

Low energy cathodoluminescence spectroscopy (CLS) employing incident electron energies in the range of a few kV or less enable measurement of electronic structure near semiconductor surfaces and interfaces. Coupled with photoluminescence spectroscopy (PL), the CLS technique has been extended to characterize electronic structure tens of nanometers below the free surface at metal-semiconductor and semiconductor-semiconductor junctions. CLS has revealed discrete, deep electronic states for clean and metallized semiconductor surfaces as a function of atomic ordering as well as vicinal surfaces as a function of misorientation. A combination of CLS and PL reveals deep level features associated with strain relaxation and dislocations at heterojunction interfaces as well as variations in epilayer growth conditions. Such observations demonstrate the existence of discrete, deep levels in the semiconductor band gap and their sensitivity to chemical and atomic structure near surfaces and interfaces. Furthermore, the energies and densities of such deep levels provide a consistent picture of Fermi level stabilization and band bending at semiconductor contacts. Finally, our results indicate that deep level CLS/PL measurements are an effective, in-situ probe of surface and interface quality.

Key Words: Cathodoluminescence, metal-semiconductor interface, semiconductor heterojunction, Schottky barrier, interface states, defects, deep levels, GaAs, InGaAs, ZnSe, dislocations, buried interface.

*Present address and address for correspondence:
Leonard J. Brillson,
Dept. Electrical Engineering and Physics,
Center for Materials Research
The Ohio State University
Columbus, OH, 43210

Telephone number: (614) 292-8015
FAX number: (614) 292-7396
E.mail: Brillson.1@osu.edu

Introduction

The electronic structure of semiconductor-metal interfaces have been the subject of considerable research aimed at understanding the processes of charge transfer and Schottky barrier formation (Brillson, 1982, 1992, 1993); Rhoderick and Williams, 1988). However, despite nearly fifty years of research, these phenomena are still far from well understood. Furthermore, the rectification which they produce is central to a wide array of electronic devices. A central feature of interface charge transfer and band bending are the electronic states localized near the interface, into and out of which charge may transfer. Researchers have employed a variety of surface science techniques to probe these localized interface states and have found that extrinsic, chemical and atomic structural features of the interface region rather than the intrinsic properties of the metal and/or the semiconductor can produce the dominant interface states (Brillson, 1982). Low energy cathodoluminescence spectroscopy (CLS) studies have provided some of the most direct evidence for such extrinsic surface and interface states and their dependence on preparation and subsequent processing (Brillson et al., 1985, 1988; Brillson and Viturro, 1988; Yacobi & Holt, 1990). Furthermore, CLS provides a unique method of probing interface states localized tens to hundreds of nanometers below a free surface. Such "buried" interfaces may in fact be altered by chemical and structural processes which are different or not present with only a few monolayers or less of adsorbate on a semiconductor surface. Indeed, CLS results provide strong evidence for an evolution of interface states with increasing (metal) overlayer thickness on a semiconductor surface (Viturro et al., 1986).

We have now extended the CLS technique, in concert with laser-induced photoluminescence (PL) spectroscopy, to a wide array of extrinsic states at semiconductor surfaces and buried interfaces. Here, we present CLS/PL results for near-surface and buried interface electronic states. In the following sections, we present a description of the luminescence techniques, near-surface state measurements from atomically-ordered and metallized surfaces and vicinal surfaces, and bulk and
buried interface states from misfit dislocations and chemically-altered heterojunctions. Also discussed are the correlation between the energies of these localized states and the interface Fermi levels. Finally, we discuss the application of these luminescence techniques to the monitoring and control of semiconductor device structures.

**Low Energy Cathodoluminescence Spectroscopy**

Low energy CLS has a number of advantages relative to other techniques in probing interface states. These include: (i) probe depths which can extend tens to hundreds of nanometers beyond the immediate surface region of adsorbed overlayer, multilayer film and/or epilayer film; (ii) variable probe depths which depend on incident beam energy; and (iii) the capability to generate free electron-hole pairs and thereby induce radiative recombination through deep levels and new band structure. Such radiative emission may be characteristic of atomic scale defects, extended structural imperfections and even new compounds. Except for metallic overlayer thicknesses beyond a few nanometers, the luminescence from these features can be detected in a backscattering geometry, permitting additional flexibility in preparing or processing such surfaces and interfaces under ultra-high vacuum (UHV) conditions. Detection through optically opaque overlayers is also possible in alternate experimental configurations.

In order to perform surface and interface experiments under controlled chemical conditions, we employed a UHV chamber equipped with surface characterization and modification tools. These tools include: a low energy (300-3000eV), glancing incidence electron gun, a monochromator and photon detector with near infrared sensitivity, and appropriate photon collection optics. Photon collection optics include a quartz or CaF$_2$ lens to collect the emitted light within the chamber and a sapphire viewport to transmit the light to a prism or grating monochromator and a detector. All spectra are normalized to the black body throughput of the optical train. For the results described here, we used a Ge photodiode (North Coast) with a low energy cut-off at 0.7 eV. InSb or PbS detectors are available with sensitivity extending to lower energies, albeit with considerably reduced detectivity. For experiments involving optical emission above 1.1 eV, photomultipliers provide detectivity orders of magnitude greater than the Ge photodiode. The near-surface and interface sensitivity derives mainly from the short penetration depth of the low energy electron beam. Furthermore, band bending near the interface/free-surface can enhance the recombination at localized sites by increasing the local density of minority carriers. We can estimate the maximum electron range and depth of maximum energy loss (e.g., maximum rate of electron-hole creation) by extrapolation of expressions derived for higher kinetic energies (Everhart and Hoff, 1971; Shea, 1984). These extrapolations are described in a previous publication (Brillson and Viturro, 1988). The maximum energy loss occurs at depths which are orders of magnitude smaller than those of conventional high keV or Mev electron beams. In order to analyze the energy dependence of CLS spectra, we maintained constant power dissipation by decreasing the incident flux inversely with beam voltage. Previous work confirms that the intensities of surface and bulk contributions to CLS spectra vary with energy in a complementary way (Brillson and Viturro, 1988). Furthermore, the high surface sensitivity and energy dependence of CLS spectra demonstrate that diffusion of beam-generated free carriers do not blur the excitation depth effect appreciably, presumably due to influence of band bending in moving minority free carriers toward surface or interface recombination centers (Brillson and Viturro, 1988).

A number of researchers have used CLS techniques previously to probe semiconductors (Brillson and Viturro, 1988; Yacoby and Holt, 1990). In 1985, Brillson and coworkers described the first use of CLS at low energies to probe metal-semiconductor interfaces. In succeeding years, CLS studies of metal-semiconductor interface states provided evidence for the metal-specific nature of such states (Viturro et al., 1986), their dependence on crystal growth (Shaw et al., 1988, 1989) and their dependence on processing (Raisanen et al., 1993; Vitomirov et al., 1992, 1992a). These results underscored the presence of discrete states at semiconductor interfaces which depend sensitively on extrinsic factors.

**Atomically-Ordered and Metallized Semiconductor Surfaces**

Studies of atomically-ordered and metallized semiconductor surfaces demonstrate the sensitivity of CLS to surface electronic states. The experiments described here were performed on clean GaAs(100) surfaces grown by MBE and analyzed under UHV conditions. By thermal decapping of a protective As overlayer, it was possible for us to transport such surfaces from the growth chamber to the UHV chamber through air and achieve LEED-ordered surfaces. Desorption and annealing at different temperatures produces a wide variety of atomic reconstructions and chemical compositions (Brillson, 1982). Figure 1 demonstrates the surface sensitivity achievable with low energy CLS. Here, deep level emission versus incident electron energy is shown for a GaAs(100) c(8 x 2) surface, obtained by annealing the epilayer at 580°C under UHV conditions. Figure 1
Luminescence spectroscopy of semiconductors

Figure 1. CLS spectra of a clean, ordered GaAs(100) (8 x 2) for excitation energies of 1, 1.5 and 2 kV. Deep level emission peaked at 1.2 eV increases with decreasing excitation range, characteristic of near-surface luminescence (Vitomirov et al., 1992a).

Figure 2. CLS spectra of a clean GaAs(100) (1 x 1) surface (bottom), with deposition of 1 nm Al (middle), and subsequent annealing at 350°C (top). Al deposition induces pronounced emission at 0.7-0.8 eV, which is removed by annealing (Vitomirov et al., 1992a).

shows a deep level emission feature which extends from the low energy detector cutoff to the near band edge emission at 1.42 eV. This emission increases with decreasing energy, particularly at energies around 1.2 eV. Such behavior is characteristic of recombination localized near the free GaAs surface. In contrast to the Ga-rich GaAs(100) (8 x 2) surface, annealing at 350°C produces an As-rich surface, which exhibits considerably less surface emission in analogous CLS spectra, indicating the influence of surface preparation on the optical emission (Vitomirov et al., 1992a).

Metallization of these GaAs surfaces results in more dramatic differences in optical emission with initial surface preparation. Such deep level emission is characteristic of the metal-semiconductor interface. Figure 2 shows that 1 nm Al on (1 x 1) surface induces pronounced additional emission at 0.7-0.8 eV. Furthermore, annealing of this interface at 410°C for 5 minutes serves to remove this metal-induced feature. Since Al reacts strongly with As on the GaAs surface, the variations in emission in these spectra indicate that changes in chemical bonding are responsible for these spectral features.

Metal-induced states at Al-GaAs(100) interfaces, in fact, exhibit a systematic dependence on the temperature of GaAs(100) surface preparation. Figure 3 illustrates difference spectra for reconstructed GaAs(100) surfaces prepared at representative temperatures. With increasing temperature, the 0.8 eV feature prominent for the (1 x 1) surface disappears, whereas the 1.2 peak feature appears only for the (4 x 6) surface. A third feature at 0.95 eV appears to be present for all three reconstructions. For Au, no such effects with temperature are observed, consistent with the qualitatively different interface chemistry (Vitomirov et al., 1992a).

The deep level emission observed for Al/GaAs(100) interfaces leads to interface states energies within the gap which correlate with observed Fermi level positions. Fermi level energies derived from soft x-ray photoemission (SXPS) data on similar reconstructed surfaces are found to vary with reconstruction, shifting from 0.84 eV to 0.96 eV, with temperature increasing from 420°C to 620°C (Vitomirov et al., 1992). Assuming that the CLS emission corresponds to transitions from states near the conduction band to acceptor states below in energy, we find a good correlation between the Fermi level positions and the deep levels, whose relative weighting of intensities shifts from 0.8 eV-0.95 eV to 1.05 eV-1.2 eV with increasing temperature over the same temperature range (this assumption for CLS emission from InGaAs and GaAs has been confirmed by surface photoconductivity (Raisanen et al., 1994) and photovoltage (Burstein et al., 1991) measurements). Thus, the interface states detected via CLS correspond
both in energy and in temperature dependence to Fermi level movements measured by SXPS.

To summarize these results for atomically ordered and metallized GaAs surface, we find: (i) multiple deep levels present near the surface and metal interface; (ii) energies and intensities which are sensitive to semiconductor temperature and reconstruction; (iii) energies and intensities which are sensitive to the chemical nature of metal overlayers; and (iv) deep level energies which correlate with independently measured Fermi level position. These results underscore the utility of CLS for studying near-surface and interface electronic structure.

Vicinal Surfaces and Interfaces

The CLS technique is also sensitive to extrinsic states associated with surface morphology (Viturro and Brillson, 1987). In this section, we show that states form within the semiconductor band gap due to presence of steps and dangling bonds at vicinal surfaces. The electronic activity of such vicinal surfaces are of practical importance since they are used to accelerate the growth of MBE films. GaAs single crystal surfaces misoriented from the [100] direction indicate significant changes in both chemical and electronic properties.

Figure 3. Difference spectra between clean GaAs(100) prepared at different temperatures and the corresponding spectra for deposition of 1 nm Al. Spectral features at 0.8 eV, 0.95 eV and 1.2 eV exhibit systematic variations with increasing temperature of clean surface preparation (Vitomirov et al., 1992).

Nanometer deposition of Al on GaAs(100) stepped surfaces leads to clear differences in the extent of chemical reaction, depending on the misorientation direction and angle. SXPS measurements of such thin Al/GaAs interfaces reveals the presence of dissociated Ga due to Al bonding with near-surface As atoms (Chang et al., 1990a). This reaction product increases with the density of active atomic sites, that is, with misorientation direction in the order [110] < [111]A < [111]B, as well as with increasing misorientation angle. Correspondingly, new interface states appear for Al on vicinal GaAs in addition to those of the oriented GaAs(100) surface. Figure 4 illustrates emission structure induced by Al deposition centered at 0.9-0.95 eV and 1.2 eV. The top difference spectrum illustrates the predominant emission at 0.9-0.95 eV for Al on stepped surface.
Luminescence spectroscopy of semiconductors

Figure 5. Self-consistent electrostatic analysis of Fermi level positions for GaAs(100) misoriented surfaces with Al and Au overlayers. The energy versus metal work function family of curves depends on the densities and energies of acceptor levels in the GaAs band gap. Curves intersecting data points provide corresponding deep level densities (Chang et al., 1990a).

These misoriented GaAs/Al interfaces also exhibit a range of band bending and corresponding Fermi level positions. Significantly, similar misoriented GaAs interfaces with Au exhibit little or no such variation (Chang et al., 1992), presumably due to the qualitative difference in interface chemistry (Brillson, 1982). From a self-consistent electrostatic analysis of Fermi level position (Duke and Mailhiot, 1986) for the different metal junctions (Chang et al., 1990a), one can derive a set of interface state densities for each misoriented surface. Figure 5 illustrates how a family of curves based only on the energies and densities of two acceptor levels fits the measured Fermi level positions. The inset shows the energies of the states required to obtain this fit, in good agreement with the optical emission energies (measured at 90 K versus room temperature) shown in Figure 4. Furthermore, the densities of these states exhibit a linear correlation with the calculated densities of active chemical sites expected for each misoriented surface, assuming an ideal lattice termination (Chang et al., 1991). This analysis indicates near-unity charge per active lattice site, a result supported by scanning tunneling microscopy studies (Pashley, 1992).

In summary, CLS studies of vicinal surfaces reveal that electronic states are present at stepped surfaces which depend on misorientation direction and step density. These states depend sensitively on metal, and their energies within the semiconductor band gap agree with a self-consistent electrostatic analysis. Finally, the CLS spectra provide an electronic description of interface states which scale with chemically-active atomic sites.

Buried Heterojunction Interfaces: Dislocations

Low energy cathodoluminescence spectroscopy has now been extended to the examination of electronic structure localized at heterojunction interfaces. In tandem with PL, one is able to excite free carriers and recombination over a large range of depths normal to the free surface and interface. It is possible, in this way, to confirm the buried interface nature of the optical emission.

Heterojunction growth involving dissimilar semiconductors with different lattice constants leads to new morphological features and associated electronic states. At low coverages, lattice mismatch is accommodated by strain and is termed pseudomorphic. Above a characteristic "critical" thickness, the epilayer lattice relaxes and forms misfit dislocations to relieve the strain (Mayer and Lau, 1990). Misfit dislocations may act as electrically
active sites such as recombination centers and deep traps. Such electrically active sites can alter dramatically the transport, electrostatic and ultimate failure rate properties of devices incorporating such interfaces.

Combined CLS and PL measurements on heterointerfaces provide both a measure of localized electronic state properties and a demonstration of the depth selectivity possible with these techniques. For InGaAs grown on GaAs by MBE, one can use the relative emission from these two materials to help calibrate the relative depth of excitation. Thus, Figure 6 illustrates the band edge peaks at 1.42 (InGaAs) and 1.51 eV (GaAs), whose relative intensity changes systematically with the type of excitation (Raisanen et al., 1994a). For 100 nm In$_{0.08}$Ga$_{0.92}$As/GaAs(100) shown in Figure 6, transmission electron (TEM) micrographs display features of partially relaxed InGaAs on GaAs corresponding to $10^3$-$10^5$ cm$^{-1}$. For In concentrations of ca.10%, critical thicknesses are in the range of a few tens of nanometers. 1 kV excitation causes near bend edge emission predominantly from the epilayer. 2 kV and HeCd laser excitation leads to a more balanced emission from both materials, and HeNe excitation produces excitation weighted substantially toward the GaAs substrate.

Figure 6 also shows a number of emission features at energies deep within the semiconductor band gaps. A number of discrete peak features are apparent at 0.76, 0.83, 0.96 and 1.22 eV. The peak at 0.83 eV appears largest for excitation centered primarily on the interface region. The remaining peaks appear for excitations extending over a range of depths and correspond to bulk trap levels. These features exhibit a significant dependence on the epilayer thickness. For 300 nm In$_{0.1}$Ga$_{0.9}$As/GaAs(100), no emission from the GaAs substrate is evident for all but the HeNe excitation, as shown in Figure 7. This is consistent with the energy-range relationship mentioned earlier and with the absorption depth of HeCd and HeNe laser photons within the InGaAs. The continued appearance of the deep levels in the absence of the GaAs emission demonstrates their InGaAs or interface origin. As expected for these thicker epilayers, dislocation-induced peaks are present in all these spectra, albeit shifted to 0.87 eV. The independent variation of peak intensities for differ-
Luminescence spectroscopy of semiconductors

Figure 8. HeCd PL spectra for InGaAs/GaAs(100) heterojunctions with increasing lattice relaxation measured via TEM. The dislocation feature at 0.83-0.87 eV increases in intensity with dislocation density (Raisanen et al., 1994b).

Different excitations demonstrate that the 0.87, 0.96 and 1.13 eV peaks are not due to the same defects since they are spatially distinct.

Specimens with increasing densities of dislocations exhibit additional evidence for the dislocation nature of the 0.83-0.87 eV peak. Figure 8 illustrates spectra for InGaAs/GaAs(100) heterojunctions with increasing lattice relaxation (and thereby dislocation density) measured via TEM. Thicknesses increase from the bare GaAs substrate to well above the critical thicknesses for dislocation formation. Likewise, the increase in relaxation for the same 100 nm epilayer thickness is due to an increase in in concentration and lattice mismatch. Figure 8 shows the 0.83 eV peak appearing in spectra for thicknesses above 200 nm and shifting to 0.87 for higher dislocation densities. On an absolute intensity scale, this deep level feature increases monotonically with dislocation density. Surface photoconductivity measurements indicate that this emission corresponds to optical transitions from near the conduction band to a level 0.83-0.87 eV below. This position agrees well with spatially-resolved electron energy loss spectroscopy results (Baison et al., 1986) and differs from previous results derived from deep level transient spectroscopy (Watson et al., 1992).

Overall, these dislocation measurements show that: (i) misfit dislocations introduce a discrete deep level near mid-gap, (ii) this deep level lies 0.83-0.87 eV below the conduction band edge, (iii) the deep level intensity increases with lattice relaxation, (iv) deep levels are localized near the heterojunction interface, (v) only minor shifts in energy occur with relaxation and composition, (vi) the CLS and PL tandem measurements provide a rich variety of electronic and spatial information on the buried interface feature.
Epitaxial Growth-Induced Deep Levels

ZnSe/GaAs heterojunctions provide a final example of electronic information extracted via luminescence from buried interfaces. Figure 9 illustrates the combined CLS and PL spectra for a 500 nm thick ZnSe epilayer grown on GaAs(100). These spectra exhibit numerous features deep within the semiconductor band gaps. Such features have not been reported previously since most luminescence measurements for this system are taken near the semiconductor band edges (Gutowski et al., 1990). The epilayer interface was grown under Zn-rich conditions, with a background Zn vs. Se pressure ratio of 10. The CLS spectra exhibit no evidence for GaAs emission, demonstrating that the features at 0.9, 1.0, 1.14 and 1.3 eV are due to the epilayer or the epilayer interfaces. Only for the more penetrating HeCd or HeNe excitations is the GaAs near band edge emission apparent. Figure 9 also illustrates that the deep level emissions vary independently with excitation depth. The 0.9, 1.0 and 1.14 eV peak features appear to decrease preferentially with depth relative to the 1.3 eV emission peak. This depth dependence is characteristic of such ZnSe epilayers for other growth conditions as well. Data such as that shown in Figure 9 can be used to show that the 1.3 eV peak increases toward the ZnSe/GaAs interface. ZnSe/GaAs growth under different growth conditions, e.g., lower Zn/Se beam pressure ratios, leads to similar deep level energies but strikingly different relative intensities (Raisanen et al., unpublished). The CLS/PL technique can also provide information on very thin epilayer structures, ranging down to thicknesses less than 5 nm. These results demonstrate the importance of growth conditions on the deep levels resident within the epilayer film and at the heterointerface. Such states are important since they can affect the heterojunction band offset between the two semiconductors (Nicolini et al., 1994).

Deep Level Luminescence Measurements and Semiconductor Devices

The measurements presented here are of utility in understanding and controlling the performance of semiconductor devices. The presence of discrete deep levels can account for the Fermi level stabilization noted for III-V compound semiconductors such as GaAs. Such extrinsic states provide a chemical basis for modeling charge transfer between metals and semiconductors. Deep levels near semiconductor-semiconductor junctions can account for variations in the local dipoles which alter the heterojunction band offsets. From such models, it may be possible to design growth and processing techniques which optimize such states to achieve desired interface properties. The strong dependence of deep levels on chemical treatments in general has led researchers to new interface preparations which have yielded much wider ranges of Schottky barrier formation (Brillson, 1992).

Such luminescence probes have utility in monitoring the preparation of real semiconductor devices as well. CLS and PL can provide an in-situ diagnostic of electronic structure during semiconductor growth and processing. Luminescence features could provide an indication of the onset of dislocations, for example, above a critical growth thickness or chemical composition, thereby serving to maintain high device yields. Luminescence detection of interface features may also provide indicators of chemical and electronic degradation during normal processing steps (e.g., etching, patterning, annealing) as well during accelerated life tests.

Conclusions

Overall, the work presented here serves to show that CLS and PL are effective probes of electronic states near surfaces and interfaces. Secondly, these deep electronic states vary sensitively with surface or interface preparation. These deep level properties support a discrete state model of Schottky barrier formation. Finally, the CLS and PL techniques provide an in-situ probe of semiconductor electronic and structural quality which may find increasing utility for actual device fabrication.

References


Brillson LJ, Viturro RE, Shaw JL, Richter HW
Luminescence spectroscopy of semiconductors


Vitomirov IM, Raisanen AD, Finnefrock AC, Viturro RE, Chang S, Brillson LJ, Kirchner PD, Pettit GD, Woodall JM (1992a) Surface and interface states for GaAs(100) (1 x 1) and (4 x 2)-c(8 x 2) reconstructions. J Vac Sci Technol A10, 749-753.


