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In situ characterization and control of compound semiconductor interfaces

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Formation of semiconductor interfaces for nano-structure devices requires an entirely UHV-based integrated fabrication/characterization system to achieve atomic-scale perfection. This paper discusses recently developed characterization and control techniques for use in such a system. The process characterization technique is based on photoluminescence and determines the surface state density distribution on processed 'free' surfaces of semiconductors. The interface control technique uses an ultrathin MBE Si interface control layer and has been applied to insulator–semiconductor, metal–semiconductor and semiconductor–semiconductor interfaces.

1. Introduction

Semiconductor nano-structures are drawing attention for future quantum devices as well as for ultimate miniaturization of conventional devices. Interfaces are basic constituent elements of any devices, and they play far more important roles in future nano-structure devices than at present. The basic motivation for interface formation in devices is to create and use potential energy differences at the interface as shown in figure 1*a*. Thus controlled fine tuning of such differences by a suitable engineering approach is obviously desirable.

Interface formation often causes creation of gap states at interface as schematically shown in figure 1*b*, leading to the so-called Fermi level pinning phenomenon. Such interface states usually cause various unwanted phenomena of shielding external fields, causing unwanted carrier depletion or accumulation, enhancing interface recombination, generating recombination-generation noise, causing drift and other instability phenomena, adversely interacting with confined quantum states causing carrier leakage and possibly causing side-gating phenomena in planar structures (Thornton *et al.* 1992).

Thus proper characterization and control of interfaces are key issues for success of nano-electronics. To achieve atomic-scale perfection of interfaces, it seems imperative to develop a completely UHV-based fabrication system where formation and characterization of interfaces are done *in situ* without air exposure. This paper discusses some of UHV-based in-situ characterization and control techniques of compound semiconductor surfaces and interfaces recently developed by my research group for use in a UHV-based system schematically shown in figure 2. The process characterization technique is based on photoluminescence (PL) and determines the surface state density distribution on processed 'free' surfaces of semiconductors. The interface control technique uses an ultrathin MBE Si interface control layer and has

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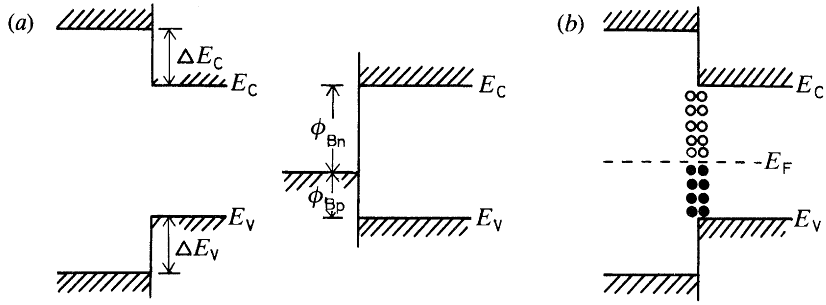

Figure 1. (*a*) Ideal interfaces and (*b*) areal interface with interface states causing Fermi level pinning.

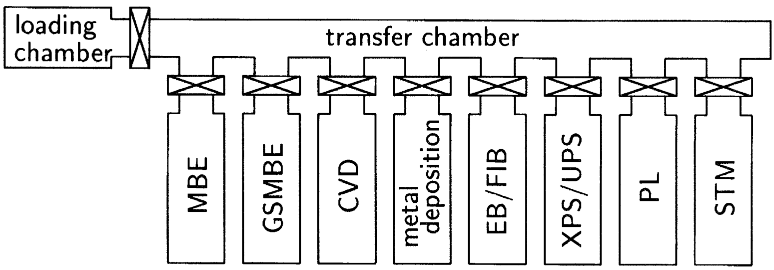

Figure 2. A schematic representation of a UHV-based fabrication characterization system used in the present study.

been applied to insulator–semiconductor (I–S), metal–semiconductor (M–S) and semiconductor–semiconductor (S–S) interfaces.

2. *In situ* process characterization by photoluminescence

(*a*) *Basic principle and experimental set-up*

The processing steps for nano-structure fabrication are generally applied to surfaces, and they produce electronically active surface or interface states, reflecting surface reconstruction or surface damages of varying characters and degrees. However, there has been no well-established technique to characterize them. The recently developed photoluminescence surface state spectroscopy (PLS^3) technique (Saitoh *et al.* 1991) allows, for the first time, *in situ*, non-destructive and contactless determination of surface state density (N_{ss}) distributions on the processed free surfaces of semiconductors.

The new PLS^3 technique consists of a detailed measurement of excitation intensity dependence of the quantum efficiency of the band-edge PL efficiency and its subsequent rigorous computer analysis (Saitoh & Hasegawa 1991).

Photoluminescence has been widely used for assessment of surfaces and quantum structures. However, the previous PL intensity analysis has been only qualitative, being based on a phenomenological description of surface recombination process in terms of a surface recombination velocity, S, and 'dead' layer width, *W* (Mettler 1977), as schematically shown in figure 3*a*. In the new technique, a rigorous computer analysis is made on the physical situation shown in figure 3*b*, using the phenomenological semiconductor equations including SRH recombination processes through a surface state continuum. Such a computer analysis has indicated that the PL quantum efficiency and the corresponding effective surface recombination

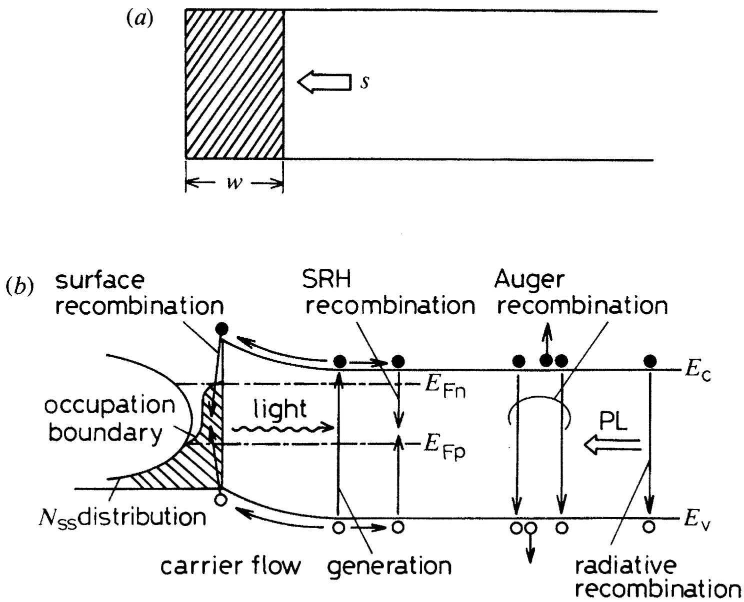

Figure 3. (*a*) Previous model for PL analysis and (*b*) the actual physical situation during PL measurement.

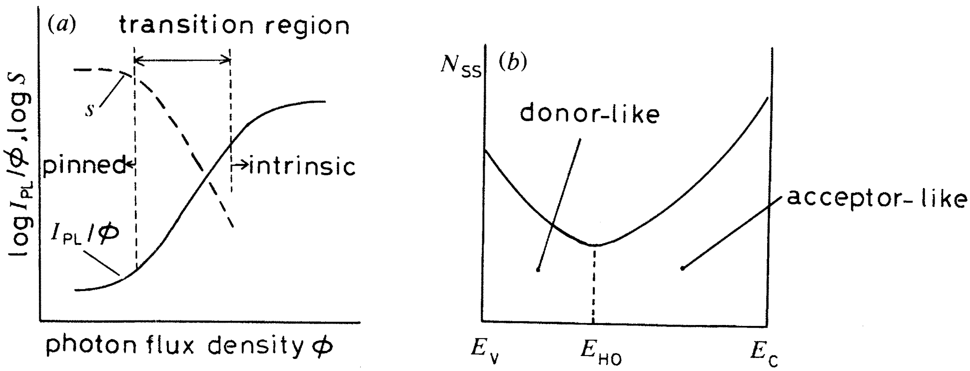

Figure 4. (*a*) General behaviour of PL quantum efficiency and (*b*) generally observed U-shaped interface state distribution with characteristic charge neutrality level.

velocity exhibit three distinct regions versus excitation intensity as shown in figure 4*a*. At low excitation intensities, the efficiency takes a low constant value which is primarily determined by the pinning position of the surface Fermi level in the dark. On the other hand, at high excitation intensities, the efficiency approaches an intrinsic value limited by the bulk radiative and Auger recombination processes. The transition region between these two limits is related to photo-induced unpinning process where the quasi-Fermi-levels for electrons and holes scan the surface states within the energy gap. Thus this region strongly reflects the N_{ss} distribution. By analysing this region rigorously by computer methods, one can determine the N_{ss} distribution. Roughly speaking, the slope of the PL efficiency gives the distribution shape, being unity for discrete states.

Table 1. *Determined minimum state density, N_{ss0}, for variously processed surfaces and regrown interfaces of* GaAs(100)

	$N_{ss0}/(\mathrm{cm^{-2}\,eV^{-1}})$
growth and processing	
as-received wafer	1.0×10^{12}
MBE growth	9.5×10^{11}
chemically etched	2.0×10^{11}
photo-CVD SiO_2 deposited	5.0×10^{11}
regrowth characterization using AlGaAs cap layer	
without interruption	2.0×10^{9}
interrupted in As_4 flux at T_g for 1 h	9.0×10^{10}
interrupted in UHV at room temperature for 4 h	2.8×10^{11}
exposed to air	9.8×10^{11}

(*b*) *Results on processed surfaces and regrown* MBE *interfaces*

N_{ss} distributions were determined on as-received, freshly MBE grown, wet and dry etched, oxidized and insulator deposited surfaces of GaAs, InP, AlGaAs and InGaAs (Sawada *et al.* 1993). Measurements were calibrated by C–V measurements on standard MIS samples. As schematically shown in figure 4*b*, the distributions were found to be generally U-shaped with their minima occurring at the hybrid orbital charge neutral level, E_{HO}, below and above which states are donor-type and acceptor-type, respectively. This is consistent with the DIGS (disorder-induced gap state) model concerning the Fermi-level pinning phenomena (Hasegawa & Ohno 1986). E_{HO} is equivalent to the midgap energy by Tersoff (1984). E_{HO} was found to lie 0.47, 1.00 and 0.47 eV above the valence band maximum for GaAs, InP and $In_{0.53}Ga_{0.47}As$, respectively. The distributions could generally be fitted well into the following empirical formula:

$$N_{ss} = N_{ss0} \exp\left(|E - E_{HO}|/E_0\right)^n. \tag{1}$$

The magnitudes of the density were found to be strongly dependent on the details of processing. The values of minimum density N_{ss0} measured on GaAs surfaces are summarized in table 1.

Growth interruption and regrowth are steps often used for fabrication of nanostructures. For characterization of MBE regrown interfaces of GaAs, an AlGaAs top layer was used to avoid complication due to co-existence of surface recombination and interface recombination (Sawada 1992). The measured PL efficiency data is shown in figure 5. Again, the state distributions were found to be U-shaped with E_{HO} and the values of N_{ss0} are summarized in table 1. Thus, well-known carrier profile anomaly associated with regrowth is definitely attributed to formation of a U-shaped interface state continuum. The present method seems to be useful for assessments of surface effects in quantum structures.

3. *In situ* control of semiconductor interfaces by Si ICL

(*a*) *Basic structures and their preparation*

The new technique for *in situ* control of interfaces utilizes an ultrathin MBE Si interface control layer (Si ICL). The basic structure and its applications to I–S, M–S and S–S interfaces are shown in figure 6. Experiments were done using the system

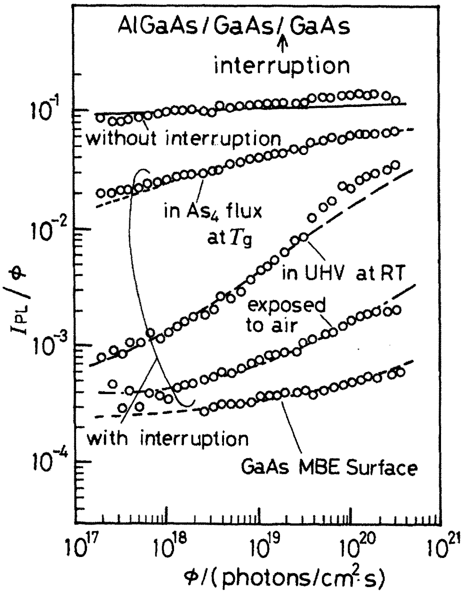

Figure 5. PL data for growth interrupted MBE GaAs interfaces.

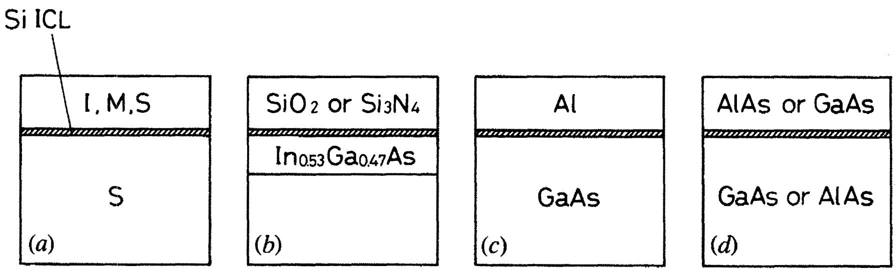

Figure 6. Interface control by Si ICL.

shown in figure 2. Processing sequence includes (1) MBE growth of InGaAs, GaAs or AlAs, (2) MBE growth of Si ICL from a Si K-cell at a substrate temperature of 250 °C (3) thermal oxidation, photo-CVD deposition (SiO_2 or Si_3N_4) using ArF excimer laser, metal deposition or growth of the semiconductor overlayer, depending on the sample structure. The growth rate of Si ICL was 20 Å h^{-1}. Doping into Si ICL was made by As and Ga both from the K-cell. RHEED pattern quickly changed from the As stabilized (2×4) pattern to (1×2) or (3×1) pattern during Si growth on GaAs, depending on whether the growth was done without As-supply or under the As stabilized condition, respectively.

(*b*) *Control of I–S interface*

The basic idea of I–S interface control (Hasegawa *et al.* 1988; Akazawa *et al.* 1991) is that the Si ICL terminates surface bonds of the compound semiconductor by a pseudomorphic array of Si atoms which make in turn a smooth transition to an outer SiO_2 layer. The necessary conditions are; (*a*) ICL should maintain pseudomorphic matching to semiconductor, (*b*) ICL should prevent direct oxidation of the semiconductor and (*c*) ICL should form a good SiO_2–Si interface with minimal suboxide components.

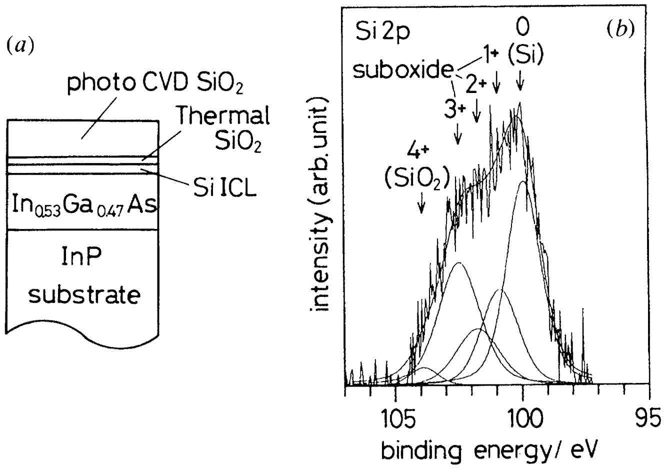

Figure 7. (*a*) Improved structure and (*b*) XPS monitor of suboxide components.

The experiments were done on $In_{0.53}Ga_{0.47}As$ surfaces. When photo-CVD SiO_2 deposition is made directly onto Si ICL, penetration of photo-excited oxygen radical exceeds its critical layer thickness. For this reason, an improved structure in figure 7*a*, involving partial thermal oxidation of Si ICL, was used. Monolayer level process monitor of suboxide components was made by *in situ* XPS. As shown in figure 7*b*, Si 2p signal separated from Ga3p signal was decomposed into suboxide components using the chemical shift data after Himpsel *et al.* (1988).

An optimized process involving a repeated deposition–oxidation–annealing cycle made simultaneous achievement of the above three conditions (*a*)–(*c*) possible, leading to N_{ss0} of $1\text{–}2\times10^{11}$ cm^{-2} eV^{-1}. Depletion mode MISFETS with the channel mobility as high as 3850 cm^2 V^{-1} S^{-1} and an extremely small current drift (below 0.7%) have been realized. Use of Si_3N_4 instead of SiO_2 resulted in results not as good as those by SiO_2.

(*c*) *Control of M–S interface*

The basic idea to control the Schottky barrier height (SBH) in the Al–Si ICL–GaAs structure in figure 6*c* is shown in figure 8*a* (Koyanagi *et al.* 1993), where the Fermi level is firmly pinned at Al–ICL interface but not pinned at the ICL–GaAs interface. For the undoped case, the band diagram becomes as shown on the top, since the pinning at Al–ICL interface and the band alignment at ICL–GaAs interface both take place at E_{HO}. When the ICL is sufficiently doped with donors, a high field resulting from ionized donors modify the SBH, as shown at the bottom. The opposite takes place if it is doped with acceptors.

Experimentally, Si ICL was doped with As or Ga both supplied from K-cells. The Fermi level positions before and after metal deposition was measured by XPS core level shifts and *C–V/I–V* analysis, respectively. Both results agreed well after taking account of the surface photovoltaic effect in XPS measurements. It was found that As doping was effective but not Ga-doping. By doping As into Si ICL to different doping levels, SBH could be precisely controlled over about 400 meV for both n- and p-type samples, as shown in figure 8*b*. The SBH value was very reproducible and the ideality factor n was close to unity ($n < 1.05$), as long as the Si ICL was about or below the estimated critical thickness of about 10 Å.

As the ICL thickness was further increased into the relaxed region, large deviations

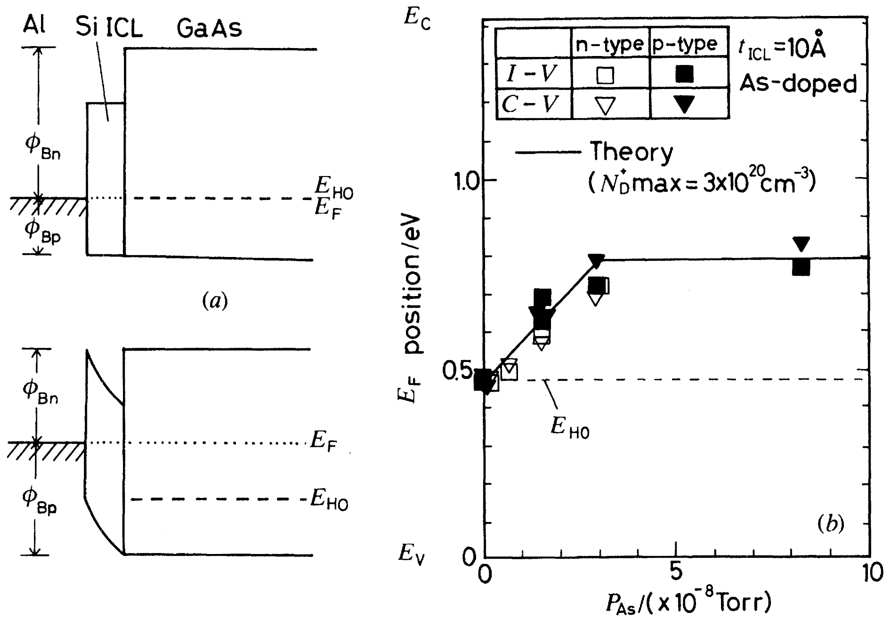

Figure 8. (*a*) Principle of SBH control by Si ICL and (*b*) SBH of Al–GaAs interface with As-doped Si ICL.

and scatter of SBH values from the ideal theory took place together with disagreement of SBH values between *C–V* and *I–V* techniques and increased ideality factors. This was explained by generation of high density interface states at the Si ICL–GaAs interface due to relaxation. This mechanism is entirely different from the previous works (Waldrop *et al.* 1988; Costa *et al.* 1991; Silberman *et al.* 1991).

(*d*) *Control of S–S interface*

The effects of insertion of Si ICL at GaAs–AlAs and InGaAs–InAlAs interfaces were investigated by XPS to investigate the feasibility of band line-up change by the ICL-induced dipole shift shown in figure 9*a*, *b* which was reported theoretically (Muñoz *et al.* 1990; Peressi *et al.* 1991) and experimentally (Sorba *et al.* 1991).

Insertion of Si ICL resulted in very large relative shifts of corelevels for GaAs–AlAs interface whose magnitudes are in excellent agreement with Sorba *et al.* (1991). Much smaller shifts were observed for InGaAs–InAlAs. However, two additional effects were observed on the XPS spectra both of which were difficult to explain by the interface dipole model. They are (*a*) anomalous increase of the energy separation between the core level (E_{CL}) and the surface valence band maxima (E_{vs}), and (*b*) anomalous increase of the FWHM of core level signals of the outer layer. The observed anomalous behaviour can be quantitatively explained by the new model without modification of ΔE_v shown in figure 9*c* (Akazawa *et al.* 1992) where the delta-doping effect combined with the near-mid-gap Fermi level pinning at surface produces a high field within the escape depth of photoelectrons which modifies the peak position and shape of the core level spectra. By assuming reasonable parameter values for delta doping taken from the recent reports, the observed values of ($E_{vs} - E_{CL}$) and FWHM increase could be completely reproduced on computer. One way to avoid Si diffusion may be use of the migration enhanced eiptaxy (MEE) growth at low temperature which is presently being investigated.

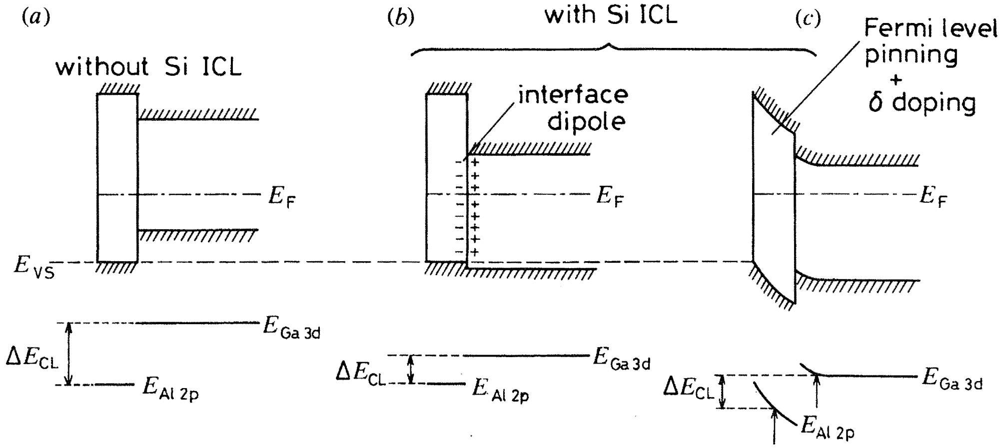

Figure 9. Band diagrams for (*a*) the interface without Si ICL; (*b*) the interface dipole model and (*c*) the delta-doped interface model.

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