

Passivation of GaAs(111)A surface by Cl termination

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It is found that an ordered and air-stable GaAs(111)A-(1×1)-Cl surface can be produced by chemical etching/passivation with dilute HCl solution. The synchrotron polarization-dependent Cl *K*-edge x-ray absorption near-edge structure and x-ray photoelectron spectroscopy studies showed that the surface is terminated with Ga-Cl bonds oriented along the surface normal. Low-energy electron diffraction studies showed a bulklike (1×1) structure on the Cl-terminated GaAs(111)A surface. The Cl termination eliminates surface band-gap states caused by surface oxides. Photoluminescence measurements showed a dramatic increase in the near-band radiative emission rate corresponding to reduction in the occupied surface band-gap states. A reduction of surface gap states by Cl termination was confirmed by surface photovoltage measurements. © 1995 American Institute of Physics.

One of the major trends in modern electronic materials and device research is to reduce individual devices down to nanoscale dimensions. At such a small scale, the total number of surface and interface atoms then becomes a significant part of the device. The passivity and stability of surface atoms are expected to control to a large degree the performance and reliability of a particular device. Even now for air-oxidized III-V surfaces, the high number of surface states and high surface recombination velocity have contributed to many failures in optoelectronic devices such as catastrophic optical mirror damage in semiconductor lasers.¹⁻⁴ Surface passivation has, for example, been found to be an absolutely essential process in the manufacturing of micro-disk lasers.⁵ Therefore, ways of removing native oxides and passivating the surface against oxidation have been actively researched in recent years both for device manufacturing and for epitaxial growth on patterned surfaces.¹⁻¹⁰ Sulfur passivation has been the most widely used passivation method since its discovery by Sandroff *et al.*⁷ For (100) surfaces, it is found that S forms bridge bonds with group-III elements¹¹⁻¹³ and, therefore, naturally saturates all dangling bond (DB) states. For a GaAs(111)A surface with Ga termination, however, each surface Ga atom has one empty DB oriented along the surface normal. Saturating these empty DBs by forming monovalent bonds with adatoms such as Cl should in principle produce a stable surface. This letter reports on our recent discovery of producing a Ga monochloride terminated GaAs(111)-(1×1) surface.

Undoped, epitaxially grown GaAs(111)A samples supplied by American Xtal Technology were used in the study. The sample preparation was based on the etching procedure reported by Lu *et al.*¹⁴ with certain modifications. In the present case, the epitaxially grown surface was immersed in dilute (10%) HCl solution at room temperature for a few minutes. As will be shown, the HCl treatment produces an oxide-free surface terminated with Cl. The Cl-terminated surface is

found to be stable in air for at least 1 h, which is the time normally required for sample transfer to ultrahigh vacuum (UHV) systems for surface structure analysis.

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition of surfaces using equipment and methodology as described in Ref. 15. The presence of Cl on the treated surface was identified by its *2p* core level with *p*_{3/2} located at 198.0 eV, as shown in Fig. 1(a). Figure 1(b) shows an As *2p*_{3/2} spectrum which can be fitted by a single Gaussian-Lorentzian peak centered at 1322.98 eV. Figure 1(c) shows a Ga *2p*_{3/2} spectrum which can be fitted by two peaks. The major peak at 1117.27 eV is attributed to Ga bonded to As, and the second peak with a chemical shift of 1.25 eV is explained as due to Ga-Cl bonding. XPS data suggest that the surface is free of Ga and As oxides and that GaCl species are present on the surface.

The chemical coordination of Cl was studied by photoelectric polarization-dependent Cl *K*-edge x-ray absorption near-edge spectroscopy (XANES) carried out on the Canadian double-crystal (InSb) monochromator (DCM) beam line located at the Synchrotron Radiation Center of the University of Wisconsin-Madison. The total electron-yield XANES spectra were obtained by measuring sample current in a vacuum chamber as described in detail in Ref. 11. The photon beam was kept at a constant 20° glancing incidence angle while the sample can be rotated along the axis parallel to the photon beam. The sample was positioned such that the sample surface [(111)-plane] could be rotated either parallel or perpendicular to the plane-polarized photoelectric vector **E** at a constant photon incidence angle. Such a sample configuration is designed to eliminate surface effects at two extreme polarizations.¹⁶

The Cl *K*-edge absorption is caused by the photon-induced transition of *K*-shell electrons to empty valence orbitals, which must be of *p* character due to the dipole transition selection rule. The prominent feature in XANES spectra from a covalent system is the transition of *s* electrons to

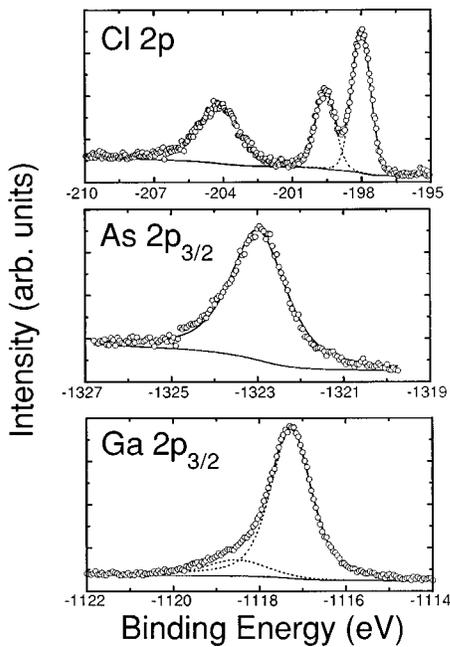


FIG. 1. Cl $2p$, As $2p_{3/2}$, and Ga $2p_{3/2}$ spectra recorded from a HCl-treated surface. The open circles are as-recorded data and the solid lines are Shirley background subtraction. For the Cl $2p$ spectrum, the two dashed lines represent spin-orbit splittings $p_{3/2,1/2}$ and the solid line is the sum of these two components. The peak at 204 eV is from the As $3s$ core level. For the As $2p_{3/2}$ spectrum, the data can be fitted by a single peak shown as the solid line. For the Ga $2p_{3/2}$ spectrum, the data can be fitted by two components positioned at 1117.27 eV due to Ga(-As) and at 1118.52 eV due to Ga(-Cl).

antibonding σ -like orbitals, which is often referred to as σ resonance. Since the bonding and antibonding states are along the same axis, σ resonance has been used extensively to determine the orientation of adatom chemical bonds on surfaces. It is well established^{11,17} that the σ -resonance intensity $I \propto \cos^2(\theta)$, where θ is the angle between the photoelectric vector and the chemical bond orientation. Figure 2 shows Cl K -edge XANES spectra taken at two different polarizations at $\theta=20^\circ$ and $\theta=90^\circ$. The data were as-recorded with a linear pre-edge background subtraction. The sharp peak at

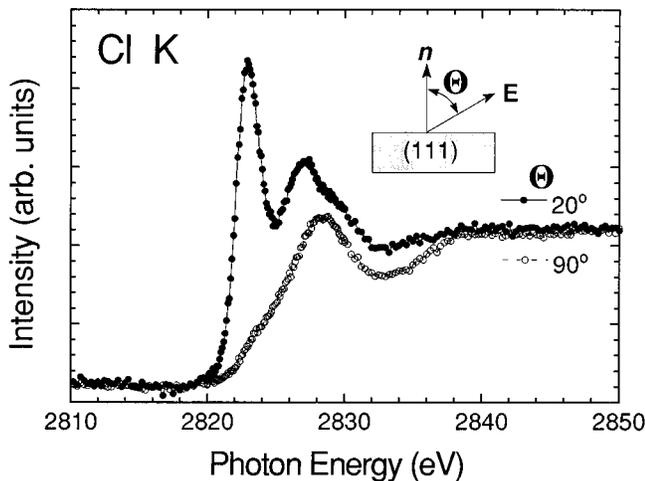


FIG. 2. Cl K -edge XANES spectra taken on a GaAs(111)A surface at two polarization angles.

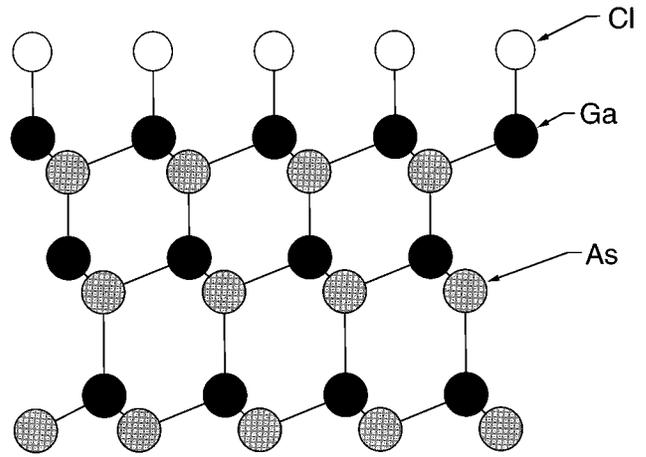


FIG. 3. Schematic view of Cl-terminated GaAs(111)A surface.

about 2823 eV is the σ_z resonance,¹⁷ caused by the transition of Cl s -electrons to Cl-Ga antibonding states. This interpretation on the nature of Cl was confirmed by measuring a GaCl₃ model compound and also by comparing the XANES spectra with previously reported data¹⁷ of Cl on Si(111) and Ge(111) surfaces where monochloride termination was also found. The XANES spectra show that the σ -resonance intensity is very strong when \mathbf{E} is tuned towards the surface normal ($\theta=20^\circ$) and resonance is very weak when \mathbf{E} is perpendicular to the surface normal. This indicates that the Cl-Ga bond is perpendicular to the (111)-plane. Based on the dipole selection rule, it may be concluded that the Ga-Cl bonding states, $|\sigma_z\rangle$, are formed between atomiclike $|\text{Cl}, p_z\rangle$, and DB $|\text{Ga}, sp^3\rangle$.

The structure of the surface was studied by LEED. A GaAs(111)A sample was passivated as described above, and transferred within 40 min into a surface analytical chamber containing a PRI RVL 8-120 reverse-view LEED. The LEED data were obtained at a chamber pressure of about 5×10^{-10} Torr. A (1×1) LEED pattern, commensurate with the underlying bulk periodicity, was obtained on as-passivated surfaces. Based on LEED, XPS, and synchrotron polarization-dependent Cl K -edge XANES measurements, however, it may be concluded that the surface is terminated by ordered Ga monochloride bonds. A schematic view of the surface is shown in Fig. 3.

The optical properties of Cl-terminated GaAs were studied using photoluminescence (PL) spectroscopy at 15 K. The excitation source was the 488 nm line of an Ar⁺ laser with pumping power of 5.7 mW. All measured spectra were recorded using a Chromex 0.5 m grating monochromator with a Si photodiode. Figure 4(a) shows the near band-gap PL spectra for a Cl-terminated GaAs(111)A surface and an untreated reference sample with a native oxide layer. PL spectra exhibit two peaks corresponding to bound-exciton (BE) recombination (with an unresolvable fine structure) at 1.52 eV and free-to-bound recombination involving carbon shallow acceptors (e, A^0) at 1.50 eV.¹⁸ After HCl treatment the intensities of both peaks are enhanced, although the enhancement for the BE peak is somewhat higher. The enhancement in PL intensity from Cl-terminated GaAs is attributed to a reduction in the concentration of nonradiative surface recombina-

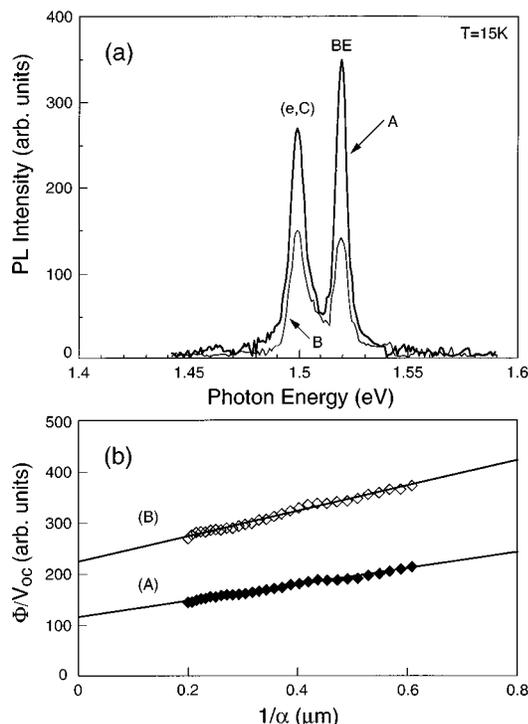


FIG. 4. (a) Near band-gap 15 K PL spectra, shown for epi-ready GaAs(111)A samples indicating bound exciton (BE) and carbon-related free-to-bound (*e*, *C*) emissions for as-received (curve B) and Cl-passivated (curve A) samples. (b) Above band-gap surface photovoltage (SPV) spectra of Cl-passivated (curve A) and unpassivated (curve B) GaAs(111)A at room temperature.

tion centers, which is usually caused by surface oxide that is removed by HCl treatment.

We also examined changes in the surface recombination behavior for GaAs(111)A surfaces due to Cl termination using steady-state surface photovoltage (SPV) spectroscopy. The SPV technique uses low-level optical excitation to generate nonequilibrium photocarriers within the sample. The open-circuit voltage between a semitransparent upper electrode and a back contact are used to reveal both charge carrier transport and surface recombination characteristics. SPV can be regarded as a “minority carrier lifetime” method for extrinsic semiconductors, where lifetime or diffusion length can be determined from the spectral dependence of the surface potential.¹⁹ In the case of undoped GaAs, however, the SPV come from different sources. Owing to the lack of free carriers under equilibrium conditions, strong energy bending is likely to occur near the surface. Thus a Dember voltage is created resulting from the difference in the diffusivities of photoexcited electrons and holes. This has been shown to dominate the SPV signals in such materials.^{19,20} For the present SPV measurement, a 100 W tungsten halogen lamp and a 0.5 m Chromex monochromator were used as the excitation light source. The details regarding the measurement are given in Refs. 19 and 20.

Figure 4(b) presents the normalized SPV (photon flux divided by photovoltage) versus inverse absorption coefficient. The ambipolar diffusion length determined from the horizontal axis intercepts^{19,20} is $0.85 \pm 0.09 \mu\text{m}$, consistent with there being no measurable change in bulk carrier properties after Cl treatment. However, the slope of the line fol-

lowing treatment is reduced compared with that for the pre-treated material; the slope ratio is proportional to the ratio of $\{S+(D/L)\}$ before and after treatment, where S is the surface recombination velocity and, D and L are the ambipolar diffusivity and diffusion length, respectively.^{19,20} Since (D/L) is constant with a value $\sim 5 \times 10^4 \text{ cm/s}$, Cl treatment results in a reduction in S of $\sim 2\text{--}3$ times.

The formation of a Ga–Cl bond rather than a Ga–H bond may be explained by thermodynamic considerations. The bond energy of Ga–Cl (481 kJ/mol) is much higher than that of Ga–H (<274 kJ/mol), of As–Cl (448 kJ/mol) and of Cl–H (431 kJ/mol).²¹ The Ga–Cl bond will, therefore, be favored energetically. By contrast, kinetics rather than thermodynamics were found²² responsible for H termination of Si surfaces after HF treatment.²³ Cl termination on (100), (110), and (111)B was also found by XANES, but the Cl bond orientation was not apparent in most cases. This may be attributed to the co-existence of several types of chlorides. Details regarding these surfaces as well as other III–V compound semiconductor surfaces will be reported later.²⁴

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