

Surface Passivation of (100)-Oriented GaAs via Plasma Deposition of an Ultrathin S-Containing Polymer Film and Its Effect on Photoluminescence

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Ultrathin S-containing polymer films of about 5 nm in thickness were deposited on the HCl-etched (100)-oriented single-crystal GaAs substrates via RF plasma polymerization of bis(methylthio)methane (BMTM). The chemical composition and structure of the BMTM plasma-polymerized GaAs(100) surface (pp-BMTM-GaAs surface) were investigated by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS), respectively. The XPS and ToF-SIMS results showed that the sulfur atoms from the plasma-polymerized BMTM (pp-BMTM) film were bonded to both the Ga and As atoms. The low-temperature photoluminescence efficiency of the so-passivated GaAs single crystal was increased by 2-fold. The growth of the oxide layer on the pp-BMTM-GaAs surface was effectively hindered for up to at least 2 months under the atmospheric conditions. The rate of surface oxidation was also reduced significantly in the presence of the pp-BMTM barrier when the HCl-etched GaAs(100) was exposed to water and H₂O₂ solution. The 180°-peel adhesion test results indicated that the pp-BMTM film adhered strongly to the GaAs(100) surface.

Introduction

GaAs is one of the most important compound semiconductors. In comparison with the Si-based devices, the compound semiconductors have advantages in radiation resistance and power dissipation.¹ However, surface recombination arising from the electron deficiency has limited the widespread application of GaAs as a compound semiconductor. To improve the performance of GaAs single crystals, considerable efforts have been made to passivate the GaAs surface.^{2–10}

In contrast to other passivation methods, passivation of GaAs surface by sulfur-containing compounds can give rise to a combined chemical and electronic passivation. The method is effective in reducing the surface recombination velocity and in the unpinning of the surface Fermi level.^{4,5} It has been shown that the formation of As₂S₃ and Ga₂S₃ is the key factor in reducing the surface recombination velocity.^{3,6} Furthermore, passivation by sulfur-containing compounds can also be used to inhibit the interdiffusion of Ga and As into the overlayer grown on the GaAs surface.^{11,12} Several fine studies have been devoted to passivation using inorganic sulfur-containing agents, such as Na₂S,^{2,3,13} (NH₄)₂S,^{3–6} or (NH₄)₂S_x^{14,15} solution. It has also been reported that some of the inorganic sulfides-passivated

GaAs surfaces are not chemically stable during storage^{3,7} and pinholes may form in the films.¹⁶ As a result, the unpinned GaAs surface is gradually oxidized in the presence of light and oxygen. Furthermore, As₂S₃ is somewhat soluble in water.¹⁷ Nevertheless, coating of GaAs with stable octadecylthiol monolayers in aqueous electrolytes has been reported.⁸

In an alternative approach, plasma-polymerized thin films of polythiophene and poly(phenylene sulfide) were used as passivating insulators.^{18–20} The modified GaAs surface showed an increase in carrier diffusion length and a reduction in surface recombination velocity. The deposited polymer can also be doped to form a junction with the semiconductor.²⁰ In general, plasma polymerization is a solvent-free process which allows the deposition of polymer films of good quality and uniformity onto various substrates and has been a particularly fruitful area of research.^{19,21–27}

In this work, thin S-containing polymer films are deposited on the HCl-etched GaAs(100) surfaces by RF plasma polymerization of bis(methylthio)methane (BMTM). The chemical composition and structure of the BMTM plasma-polymerized GaAs(100) surface (the pp-BMTM-GaAs surface) and the interaction of the plasma-polymerized BMTM film (pp-BMTM film) with the GaAs surface are characterized by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The effectiveness of the

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pp-BMTM film in restraining oxidation of the GaAs surfaces under various environments, such as ambient air, water, and H_2O_2 solution, are studied by XPS analysis of the polymer–semiconductor interface. The adhesion of the pp-BMTM film with the GaAs(100) substrate is evaluated by the 180°-peel adhesion test.

Experimental Section

Materials. (100)-oriented GaAs single-crystal wafers, having a thickness of about 300 μm and a diameter of about 50 mm, were obtained from Wafer World Inc., Ft. Lauderdale, FL. The as-received wafers were polished on one side and doped with Si to a resistivity level of 0.09–0.026 $\text{ohm}\cdot\text{cm}$. The GaAs wafers were sliced into strips of 5 mm \times 5 mm in area. To remove the organic residues from the surfaces, the GaAs substrate was sonicated in ethanol for 10 min and then blow-dried with argon. The GaAs substrate was subsequently dipped into concentrated HCl (37 vol %) for 2 min to remove the native oxide layers on the surface.⁸ H_2O_2 (30 vol %) was purchased from Merck Chemical Co., Darmstadt, Germany, and was used as received. Bis(methylthio)methane (BMTM) was purchased from Aldrich Chemical Co. of Milwaukee, WI. The chemical structure of BMTM is given by $\text{CH}_3\text{--S--CH}_2\text{--S--CH}_3$.

Plasma Polymerization. Plasma polymerization and deposition were carried out on the Plasmalab 80 Plus PECVD system manufactured by Oxford Instruments Plasma Technology of Yatton, United Kingdom. The RF generator was operated at a frequency of 13.56 MHz. The plasma deposition process was performed between two circular parallel plate electrodes of 24 cm in diameter and 6 cm in separation. The GaAs(100) samples were placed on the ground electrode and the BMTM monomer at room temperature was introduced into the deposition chamber by an argon-carrier gas stream. The monomer-carrier gas mixture was then allowed to flow evenly into the reactor from a distributor embedded in the upper electrode. In all cases, the carrier gas stream was assumed to be saturated with the BMTM monomer, as dictated by the partial pressure of the latter. The glow discharge was ignited at an RF power of 50 W, a system pressure of 600 mTorr, and a gas flow rate of 30 sccm. The plasma polymerization and deposition on the GaAs surfaces was allowed to proceed for 4 s to give rise to a film thickness of about 5 nm. The film thickness was extrapolated from the thickness of the films deposited under the prescribed glow discharge conditions over a range of time intervals, on the basis of the empirical linear relation of $d = 1.1t + 0.5$, where d was the thickness in nm (up to a maximum thickness of 70 nm) and t was the deposition time in seconds. The thickness of the latter films was determined on an Alpha-STEP 500 Surface Profiler. For films used for the 180°-peel adhesion test, the deposition time was extended to 10 s to give rise to a film thickness of about 12 nm. The plasma-polymerized BMTM polymer film is referred to as the pp-BMTM film and the pp-BMTM deposited GaAs substrate is referred to as the pp-BMTM-GaAs substrate.

Surface Oxidation of the GaAs(100) Substrates. Surface oxidation of the HCl-etched and plasma-polymerized GaAs(100) substrates was carried out by exposing the samples to various environments, including ambient air (25 °C and 65% relative humidity), an aqueous medium, and hydrogen peroxide (H_2O_2) solution, for a predetermined period of time.

Surface and Interface Characterization. The chemical compositions of the pristine, HCl-etched, and passivated GaAs surfaces were determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out on the Kratos AXIS HSi spectrometer (Kratos Analytical Ltd., Manchester,

England) with a monochromatized Al K α X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The anode voltage and current were set at 15 kV and 10 mA, respectively. The pressure in the analysis chamber was maintained at 5×10^{-8} Torr or lower during each measurement. The samples were mounted on the sample stubs by means of double-sided adhesive tapes. The core-level signals were obtained at a photoelectron takeoff angle (with respect to the sample surface) of 90°. All binding energies (BEs) were referenced to the neutral carbon peak component at 284.6 eV. In curve fitting, the line width (full width at half-maximum or fwhm) for the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to $\pm 5\%$. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

The topography of the surface-modified GaAs was characterized using a Nanoscope IIIa atomic force microscope (AFM). All images were obtained in air using the tapping mode under a constant force (scan size: 5 $\mu\text{m} \times 5 \mu\text{m}$, set point: 3.34 μV , scan rate: 1.0 Hz).

The time-of-flight secondary ion mass spectrometry (ToF–SIMS) analyses were carried out on an ION-TOF SIMS IV instrument (ION-TOF, GmbH, Münster, Germany). The primary ion beam (10 keV Ar^+) with a spot size of $\sim 50 \mu\text{m}$ was rastered over an area of 500 $\mu\text{m} \times 500 \mu\text{m}$ while keeping the total dose under 10^{13} ions/ cm^2 . The pressure in the analysis chamber was maintained at 1.0×10^{-9} Torr or lower during each measurement. To reduce the charging effect, an electron flood gun was used for the charge neutralization. The calibration of the mass spectra was based on the built-in mass library.

FTIR Measurements. The pp-BMTM samples for the Fourier transform infrared (FTIR) spectroscopy measurements were obtained by direct plasma polymerization and deposition of BMTM on the freshly pressed KBr disks for about 7 min. The FTIR spectra were recorded in air on a Bio-Rad FT-IR, Model 400, spectrophotometer. Each spectrum was collected by cumulating 30 scans at a resolution of 8 wavenumbers.

PL Measurements. The photoluminescence (PL) was studied at a low temperature (14 K) in a closed cycle He cryostat. The 488 nm Ar^+ laser was used as the excitation source. The luminescence signal was dispersed by a 0.75-m monochromator and detected by a cooled photomultiplier tube. Standard lock-in technique was employed to enhance the signal-to-noise ratio.

Adhesion Strength Measurements. The adhesion strength of the pp-BMTM film to the HCl-etched GaAs substrates was evaluated by the 180°-peel adhesion test. A copper foil adhesive tape was applied to the pp-BMTM-GaAs surface and subsequently peeled off on an Instron 5544 tensile tester from the Instron Corporation of Canton, MA. The peel tests were carried out at a cross-head speed of 10 mm/min. The copper foil adhesive tape was a product of the Electron Microscopy Science Inc. of Fort Washington, PA. The adhesion strength reported was the average of at least three sample measurements. The values of the adhesion strength among these measurements usually did not vary by more than ± 0.5 N/cm.

Results and Discussion

Chemical Composition of the Pristine and Modified GaAs(100) Surfaces. Figure 1 shows the respective C 1s core-level and wide scan spectra of the pristine (as-received) GaAs(100) surface (part a), the GaAs(100) surface after being

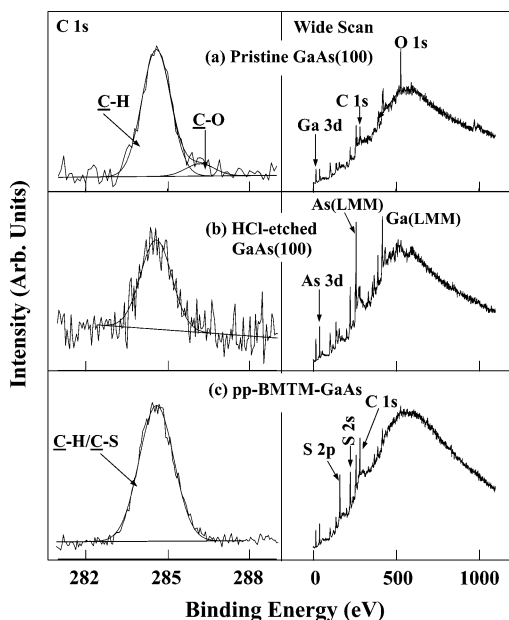


Figure 1. XPS C 1s core-level and wide scan spectra of (a) the pristine GaAs(100) surface, (b) the HCl-etched GaAs(100) surface, and (c) the pp-BMTM-GaAs surface.

etched in concentrated HCl solution for 2 min (part b), and the HCl-etched GaAs(100) surface after plasma polymerization of BMTM (the pp-BMTM-GaAs surface, part c). The intensity of the C 1s core-level spectrum of the pristine GaAs(100) surface is relatively weak and consists of two peak components, with binding energies (BEs) at 284.6 eV for the C–H and C–C species and at 286.2 eV for the C–O species. The carbon species on the pristine GaAs(100) surface are probably associated with the adventitious hydrocarbon contamination. The C 1s core-level spectrum of the HCl-etched GaAs(100) surface is barely discernible and consists of only one peak component at the BE of 284.6 eV, associated with the C–H and C–C species. Furthermore, the O 1s signal in the corresponding wide scan spectrum has disappeared after the HCl treatment. These results suggest that HCl treatment can effectively remove the native oxide layer and most of the adsorbed carbon species on the GaAs(100) surface.

The C 1s core-level spectrum of the pp-BMTM-GaAs surface can be curve-fitted with one peak component at the BE of 284.6 eV for the C–H and C–S species.²⁸ Strong S 2p and S 2s signals are detected in the corresponding wide scan spectrum. The As 3d and Ga 3d signals are still discernible in the wide scan spectrum of the pp-BMTM-GaAs surface. This result indicates that the thickness of the deposited pp-BMTM layer is below the probing depth of the XPS technique (≤ 7.5 nm for an organic matrix at a photoelectron takeoff angle of 90°).²⁹ The small pp-BMTM film thickness allows the underlying pp-BMTM/GaAs interface to be studied by XPS.

Chemical Structure of the pp-BMTM Film. Figure 2 shows the FTIR spectra of the BMTM monomer and the plasma-deposited BMTM polymer. The FTIR spectrum of the BMTM monomer shows the (RS)–CH₃ symmetric and asymmetric stretching mode at about 2914 cm⁻¹ and 2976 cm⁻¹, respectively.³⁰ The absorbance band at 1428 cm⁻¹ is assigned to the (RS)–CH₃ asymmetric deformation or the (R)–CH₂–(S–C) deformation mode.³⁰ The bands at about 984 and 740 cm⁻¹ correspond, respectively, to the CH₃ and CH₂ rocking vibration.³⁰ The spectrum of the pp-BMTM film shows characteristic absorption bands similar to those of the BMTM. The absorption band at about 965 cm⁻¹ is probably associated with the vinyl

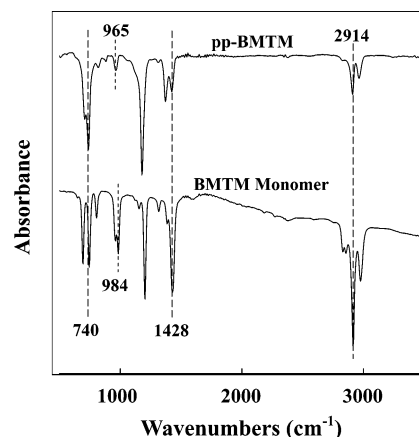


Figure 2. FTIR spectra of BMTM and pp-BMTM.

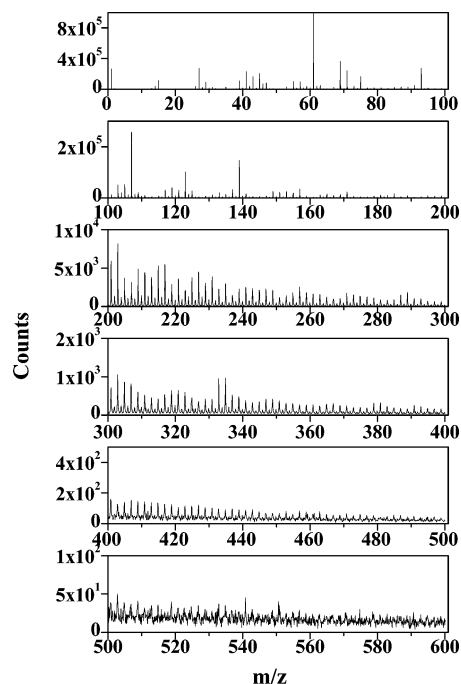


Figure 3. ToF-SIMS spectrum of pp-BMTM-GaAs surface and the assignment of the positive ion fragments.

group in R–S–CH=CH₂,³⁰ suggesting the formation of unsaturated structures in the deposited films. The relative intensity of the various CH₃ absorption modes decreases in the FTIR spectrum of pp-BMTM, as a result of the plasma polymerization. The plasma polymerization probably has proceeded via two paths: elimination of the hydrogen atoms and the C–C bond scission. Hydrogen elimination is considered to be the main reaction mechanism in plasma polymerization.³¹ The radicals are formed by the elimination of hydrogen atoms from the BMTM monomer molecules. These radicals recombined and rearranged to form polymer molecules, which contain less CH₃ groups than the total number of CH₃ groups in the starting BMTM monomer units. Arising from strong interactions of the sulfur atoms of activated BMTM molecules with the surface Ga and As atoms (see ToF-SIMS and XPS data below), as well as the fact that the plasma deposition was carried out under a relatively low pressure of BMTM and low RF power, the polymerization reaction probably had occurred predominantly at the gas–solid interface rather than in the gas phase.²⁹

Figure 3 shows the ToF-SIMS spectrum of the pp-BMTM-GaAs surface. Because hydrogen elimination is the main process during plasma polymerization, the ToF-SIMS spectrum of the

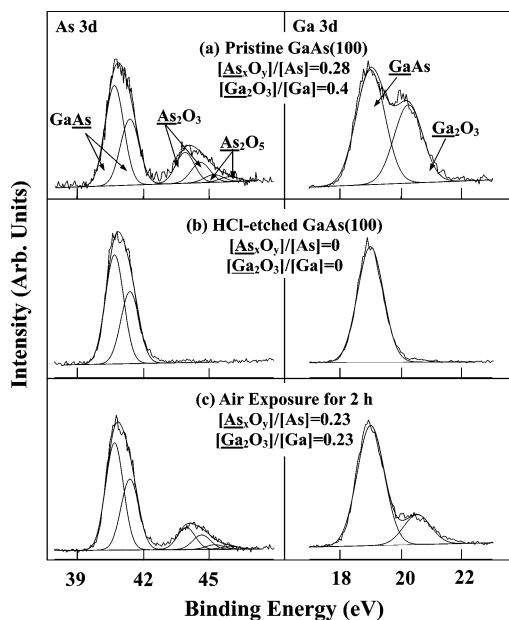
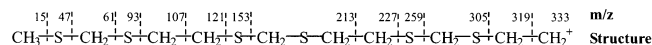
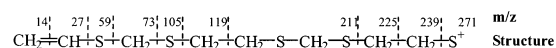
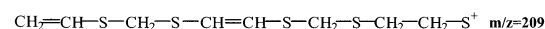


Figure 4. XPS As 3d and Ga 3d core-level spectra of (a) the pristine GaAs(100) surface and the HCl-etched GaAs(100) surfaces after exposure to air for (b) 0.1 h and (c) 2 h.

pp-BMTM-GaAs surface contains mass fragments of the BMTM repeat units, as shown in the scheme below:

SCHEME 1



In addition, several sulfur-containing species, as well as species containing unsaturated bonds, are also observed in the ToF-SIMS spectrum. The assignments of these positive ions are included in Figure 3. The fragment with an m/z value of 103 is assigned to the $\text{Ga}-\text{S}^+$ species. The peak component with an m/z value of 107 is assigned to both the $\text{As}-\text{S}^+$ and $\text{CH}_3\text{SCH}_2\text{SCH}_2^+$ fragments. Similarly, the peak component with an m/z value of 139 arises from the combined contributions of the AsS_2^+ and $\text{CH}_3\text{SCH}_2\text{SCH}_2\text{S}^+$ fragments. Thus, the formation of $\text{Ga}-\text{S}$ and $\text{As}-\text{S}$ bonds at the polymer-semiconductor interface is also verified by the ToF-SIMS results.

Oxidation of the HCl-Etched and the BMTM Plasma-Polymerized GaAs(100) Surfaces under Atmospheric Conditions. Restraint of surface oxidation of GaAs is of great importance to the application of the compound semiconductor in microelectronics, optoelectronics, and even as the electrodes, since both the As oxides and Ga oxides are unstable under ambient conditions.^{20,32} From the practical point of view, effective passivation of the GaAs surface would be to replace the native oxide layer by a stable and durable protective barrier to prevent surface oxidation in the atmosphere. Thus, the stability of the pp-BMTM passivated GaAs(100) surfaces under atmospheric conditions is first investigated.

Figure 4 shows the respective As 3d and Ga 3d core-level spectra of the pristine GaAs surface (part a) and the HCl-etched GaAs(100) surfaces after exposure to ambient air ($\sim 25^\circ\text{C}$ and 65% relative humidity) for about 0.1 h (time required to transfer the sample into the XPS chamber, part b), and 2 h (part c). The As 3d core-level spectrum of the pristine GaAs surface (Figure

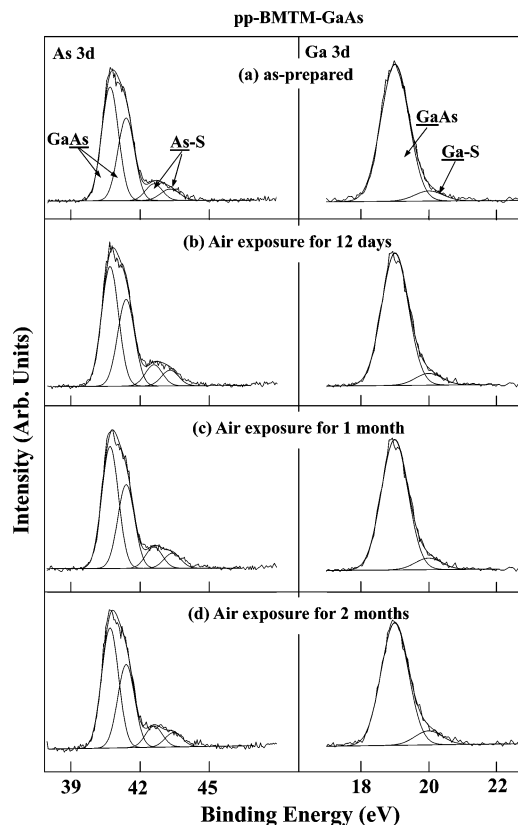


Figure 5. XPS As 3d and Ga 3d core-level spectra of (a) the as-prepared pp-BMTM-GaAs surface and the pp-BMTM-GaAs surfaces after exposure to air for (b) 12 days, (c) 1 month, and (d) 2 months.

4a) shows three spin-orbit-split doublets, having BEs at about 40.7 eV ($3d_{5/2}$) and 41.4 eV ($3d_{3/2}$) for the GaAs species, at about 44.0 eV ($3d_{5/2}$) and 44.7 eV ($3d_{3/2}$) for the As_2O_3 species and at about 45.3 eV ($3d_{5/2}$) and 46.0 eV ($3d_{3/2}$) for the As_2O_5 species.^{17,33} The Ga 3d core-level spectrum of the pristine GaAs surface can be curve-fitted with two peak components, having BEs at 19.0 eV for the GaAs species and at 20.4 eV for the Ga_2O_3 species.³ The concentration of the As oxide species on the GaAs surface is defined as the $[\text{As}_2\text{O}_3]/[\text{As}]$ ratio and is derived from the ratio of the sum of the As_2O_3 and As_2O_5 spectral component areas to the As 3d spectral area. Similarly, the concentration of the Ga oxide species on the GaAs surface is defined as the $[\text{Ga}_2\text{O}_3]/[\text{Ga}]$ ratio. The presence of As oxides and Ga oxides with concentrations as high as 0.28 and 0.4, respectively, is attributable to the native oxides. The As and Ga oxides are removed almost completely after immersion in concentrated HCl solution for 2 min (Figure 4b). However, the oxide species on the HCl-etched GaAs surface have reappeared to a large extent within 2 h of air exposure. The concentration of both oxides increases sharply from almost 0 to about 0.23, indicating that the HCl-etched GaAs surface is unstable under the atmospheric conditions.

The As 3d spectra of the pristine and air-exposed pp-BMTM-GaAs surface (Figure 5a–5d, left-hand side) all consist of two spin-orbit-split doublets, having BEs at about 40.7 eV ($3d_{5/2}$) and 41.4 eV ($3d_{3/2}$) for the GaAs species and at about 42.6 eV ($3d_{5/2}$) and 43.3 eV ($3d_{3/2}$) for the $\text{As}-\text{S}$ species.^{3,4} The corresponding Ga 3d spectra (Figure 5a–5d, right-hand side) show two peak components at the BEs of about 19 eV for the GaAs species and at about 19.9 eV for the $\text{Ga}-\text{S}$ species. The XPS results suggest that stable As–S and Ga–S bonds are formed at the pp-BMTM/GaAs interface. These results, together with the presence of $\text{Ga}-\text{S}^+$ and $\text{As}-\text{S}^+$ fragments in the ToF–

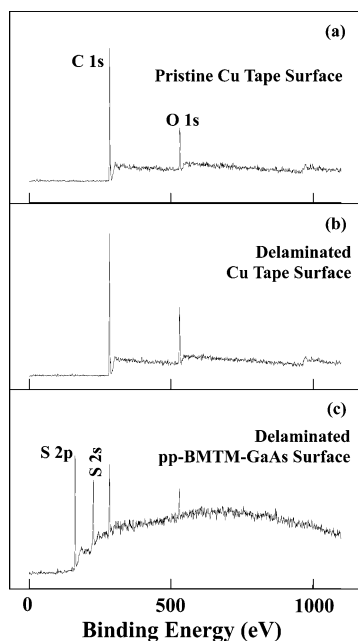


Figure 6. XPS wide scan spectra of (a) the pristine Cu tape surface, and the delaminated (b) Cu tape surface and (c) pp-BMTM-GaAs surface from a Cu tape/pp-BMTM-GaAs(100) laminate.

SIMS spectrum of the pp-BMTM surface, ready suggest that the surface Ga and As atoms have reacted preferentially with the S atoms of the activated BMTM molecules or fragments. No peak components associated with the As or Ga oxides are discernible even after 2 months of air exposure, suggesting that the ultrathin pp-BMTM layer can effectively prevent the surface oxidation of the GaAs substrate under the atmospheric conditions. The effective passivation of the GaAs surface by the pp-BMTM film is thus attributable to the formation of stable As—S and Ga—S bonds at the interface.

The formation of covalent bonds between the pp-BMTM layer and the GaAs surface is further verified by the 180°-peel adhesion test results. Generally, good adhesion is judged, qualitatively, by passing the Scotch tape peel test.³⁴ For the present work, the Scotch tape was replaced by the copper foil adhesive tape, since the latter exhibited an even better adhesion with the deposited films. The copper foil adhesive tapes were applied to the pp-BMTM-GaAs surface and subsequently peeled off on the tensile tester. The chemical compositions of the delaminated pp-BMTM-GaAs surface and the delaminated copper tape surface were analyzed by XPS. Figure 6 shows the respective wide scan spectra of the pristine copper tape surface and the delaminated pp-BMTM-GaAs and copper tape surfaces from a copper tape/pp-BMTM-GaAs laminate having a 180°-peel adhesion strength of about 3 N/cm. The wide scan spectrum of the delaminated copper tape surface is similar to that of the original copper tape surface, and no sulfur signal is discernible. The wide scan spectrum of the delaminated pp-BMTM-GaAs surface is dominated by sulfur signals, as in the case of the freshly prepared pp-BMTM-GaAs surface. The oxygen signal in the wide scan spectrum of the delaminated pp-BMTM-GaAs surface may have originated from the adhesive residues from the Cu tape surface. Thus, the copper tape/pp-BMTM-GaAs assembly has delaminated by adhesional failure at the interface between the copper adhesive tape and the pp-BMTM surface. This result indicates that the pp-BMTM layer adheres strongly to the GaAs substrate. The peel-test results are thus consistent with the presence of covalent bonds between the pp-BMTM layer and the GaAs substrate.

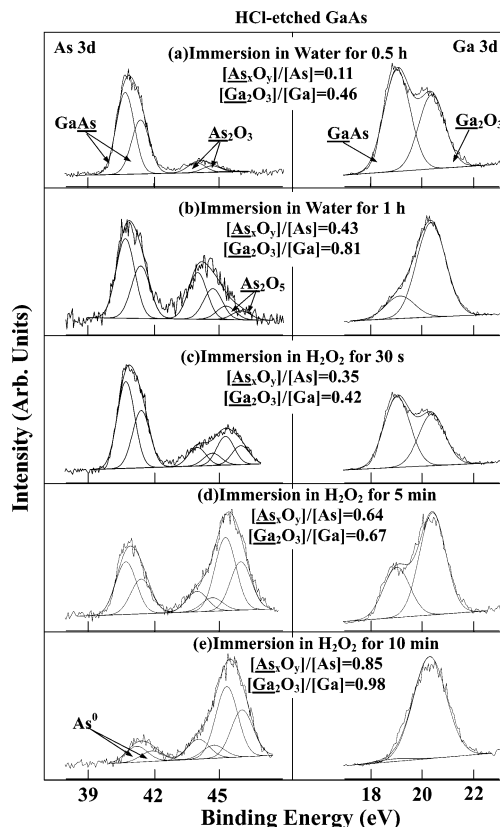


Figure 7. XPS As 3d and Ga 3d core-level spectra of the HCl-etched GaAs(100) surfaces after immersion in water for (a) 0.5 h, (b) 1 h, and after immersion in 30 vol % H_2O_2 solution for (c) 30 s, (d) 5 min, and (e) 10 min.

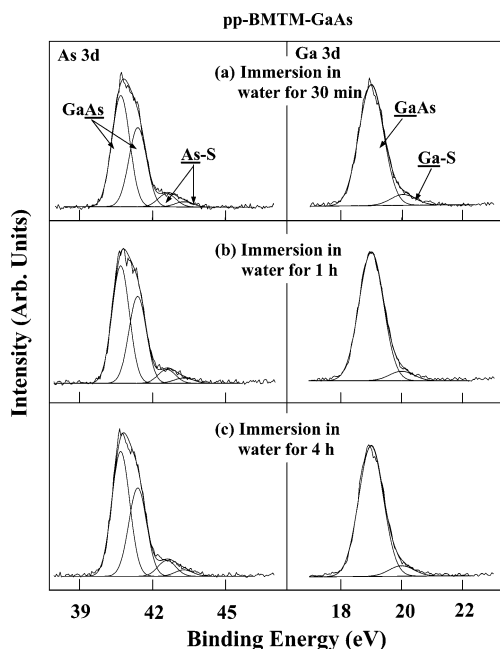


Figure 8. XPS As 3d and Ga 3d core-level spectra of the pp-BMTM-GaAs surface after immersion in water for (a) 0.5 h, (b) 1 h, and (c) 4 h.

Oxidation of the HCl-Etched and the BMTM Plasma-Polymerized GaAs(100) Surfaces in Water. Figure 7 shows the respective As 3d and Ga 3d core-level spectra of the HCl-etched GaAs surfaces from immersion in water for 0.5 h (part a) and 1 h (part b). Immersion in water for 1 h has resulted in a high concentration of both the As oxides and the Ga oxides on the GaAs surface.

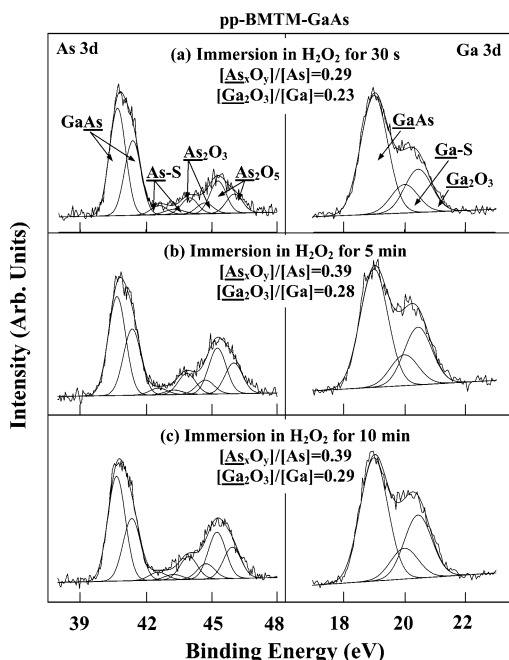


Figure 9. XPS As 3d and Ga 3d core-level spectra of the pp-BMTM-GaAs surface after immersion in H_2O_2 solution for (a) 0.5 min, (b) 5 min, and (c) 10 min.

Figure 8 shows the respective As 3d and Ga 3d core-level spectra of the pp-BMTM-GaAs surfaces after immersion in water for 0.5 h (part a), 1 h (part b), and 4 h (part c). In comparison with the As 3d and Ga 3d core-level spectra of the as-etched surface (Figure 4b), no significant increase in concentration of the oxide species is discernible on the pp-BMTM-GaAs surface after 4 h of immersion in water. Furthermore, the As-S and Ga-S bonds are stable in an aqueous environment. The XPS results thus suggest that the ultrathin pp-BMTM film can effectively passivate the GaAs surface from oxidation and hydrolysis in water. As a result, the composition mismatch of the GaAs wafer in an aqueous environment can be kept to a minimum.

Oxidation of the HCl-Etched and the BMTM Plasma-Polymerized GaAs(100) Surfaces in the H_2O_2 Solution. H_2O_2 solutions have been widely used as the oxidizing agent for GaAs. The surface oxidation behavior of the HCl-etched GaAs(100) and the pp-BMTM-GaAs(100) substrates after being immersed in H_2O_2 (30 vol %) solution for an extended period of time is compared.

Figure 7c–7e shows the As 3d and Ga 3d core-level spectra of the HCl-etched GaAs surfaces after being immersed in the H_2O_2 solution for 30 s (part c), 5 min (part d), and 10 min (part e). A substantial increase in concentration of the surface oxides is observed for the as-etched GaAs(100) substrate after immersion in the H_2O_2 solution for only 30 s. The concentrations of the As oxides and the Ga oxides on the GaAs(100) surface increase with the immersion time. The GaAs species in the surface region is almost completely oxidized after 10 min of immersion in the H_2O_2 solution. This result suggests that the thickness of the oxidized layer is comparable to the probing depth of the present XPS technique (~ 3 nm in the inorganic matrix³⁵). Furthermore, the persistence of the As^0 species (at BEs of 41.5 and 42.2 eV) after 10 min of immersion in the H_2O_2 solution is probably due to the fact that the As oxides can react with GaAs to form the As^0 and Ga_2O_3 species.^{9,36} As a result, only the complete oxidation of the Ga species in the surface region is observed.

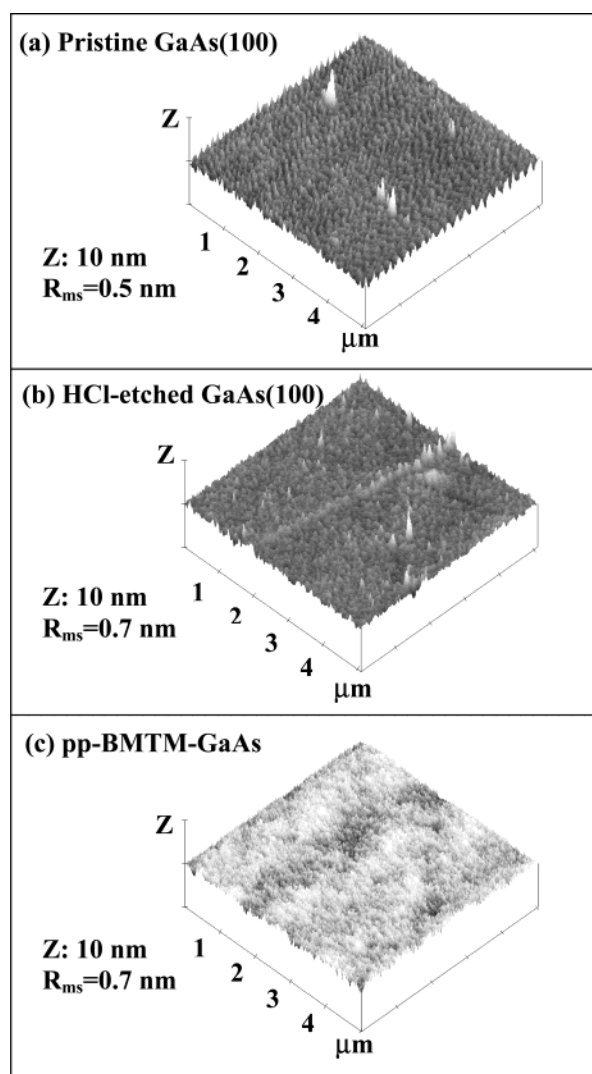


Figure 10. AFM images of (a) the pristine GaAs(100) surface, (b) the HCl-etched GaAs(100) surface, and (c) the pp-BMTM-GaAs surface.

The As 3d and Ga 3d core-level spectra of the corresponding pp-BMTM-GaAs surfaces after immersion in H_2O_2 are shown in Figure 9. An increase in As oxides and Ga oxides concentration on the pp-BMTM-GaAs surface is observed after 30 s of immersion in the H_2O_2 solution. The As_xO_y and Ga_2O_3 concentration on the pp-BMTM-GaAs surface increases to 0.39 and 0.28, respectively, after immersion in the H_2O_2 solution for 5 min. The amounts of As and Ga oxides did not increase further after prolonging the H_2O_2 exposure time to 10 min, indicating that further oxidation was retarded. The XPS results thus suggest that the ultrathin pp-BMTM layer, in combination with the newly formed oxide layer, can greatly hinder the oxidation of the GaAs surface in the presence of a strong oxidizing agent.

Surface Topography. In semiconductor processing, the preparation of a molecularly flat surface is essential to the precise control of ultrafine structures.³⁷ The changes in surface topography with surface treatments may have significant effects on the formation of interfacial states during the fabrication of devices. The surface topography of the GaAs(100) surfaces at the cleaning and passivation stages was characterized by atomic force microscope (AFM). Figure 10 shows AFM images of the pristine GaAs(100) surface, the HCl-etched GaAs(100) surface, and the pp-BMTM-GaAs surface. The pristine GaAs(100)

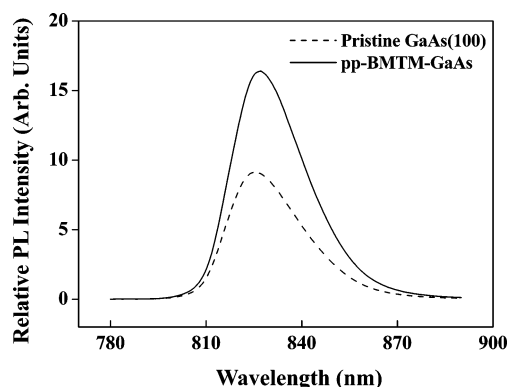


Figure 11. The photoluminescence spectra of the pristine GaAs (100) surface and the pp-BMTM-GaAs surface.

surface exhibits a rather smooth surface with a root-mean-square surface roughness (R_{ms}) of about 0.5 nm. After HCl etching for 2 min, the R_{ms} value increased slightly to about 0.7 nm. The deposition of pp-BMTM layer on the HCl-etched GaAs(100) surface did not give rise to a further increase in surface roughness. The R_{ms} value for the pp-BMTM-GaAs surface remains at about 0.7 nm. The AFM images thus suggest that the BMTM plasma polymerization process can produce a uniform and relatively smooth passivation layer.

Photoluminescence. From the optoelectronics application point of view, passivation of the GaAs(100) surface must result in a reduction in the density of surface states and the non-radiative surface recombination velocity. Previous studies have suggested that the surface oxides and the elemental As are responsible for the high concentration of midgap defects associated with the GaAs surface.^{18,38} The presence of midgap states is known to quench the photoluminescence (PL). Thus, the PL intensity enhancement in GaAs is widely used to assess the surface quality after the surface treatment procedures.^{19,36} The PL spectra of the pristine GaAs(100) surface and the pp-BMTM-GaAs surface are presented in Figure 11. An enhancement of the PL intensity by a factor of about 2 was observed at 14 K in the presence of the passivating pp-BMTM layer. Furthermore, the spectral line shape and peak position do not change after the passivation. The enhancement of the PL intensity is attributable, at least in part, to the fact that the native oxides on the GaAs surface have been replaced by the covalent Ga–S and As–S bonds. As a result, the density of surface states is reduced and the Fermi-level pinning is removed. The reduction in surface recombination velocity readily gives rise to the improved PL performance.

Conclusions

The surface of the HCl-etched GaAs(100) wafer could be effectively passivated by plasma polymerization and deposition of an ultrathin S-containing polymer film (pp-BMTM) of about 5 nm in thickness. Strong covalent bonds were formed between the sulfur atoms from the pp-BMTM layer and the GaAs surface. Because of the formation of Ga–S and As–S bonds, the growth of the oxide layer was effectively inhibited when the HCl-etched GaAs was exposed to the ambient air for up to 2 months. The pp-BMTM film even significantly retarded the surface oxidation of the HCl-etched GaAs substrate in water and in the H_2O_2 solution. In the presence of the deposited pp-BMTM layer and the accompanied reduction in surface states and recombination velocity, the low-temperature photoluminescence efficiency of GaAs was enhanced by a factor of 2.

References and Notes

- (1) Shur, M. In *Introduction to Semiconductor Technology, GaAs and Related Compounds*; Wang, C. T., Ed.; John Wiley: New York, 1990; p 27.
- (2) Sandroff, C. J.; Nottenburg, R. N.; Bischoff, J.-C.; Bhat, R. *Appl. Phys. Lett.* **1987**, *51*, 33.
- (3) Sandroff, C. J.; Hegde, M. S.; Chang, C. C. *J. Vac. Sci. Technol., B* **1989**, *7*, 841.
- (4) Cowans, B. A.; Dardas, Z.; Delgass, W. N.; Carpenter, M. S.; Melloch, M. R. *Appl. Phys. Lett.* **1989**, *54*, 365.
- (5) Carpenter, M. S.; Melloch, M. R.; Dungan, T. E. *Appl. Phys. Lett.* **1988**, *53*, 66.
- (6) Kang, M. G.; Park, H. H. *Vacuum* **2002**, *67*, 91.
- (7) Losurdo, M.; Capezzuto, P.; Bruno, G.; Perna, G.; Capozzi, V. *Appl. Phys. Lett.* **2002**, *81*, 16.
- (8) Adlkofer, K.; Tanaka, M. *Langmuir* **2001**, *17*, 4267.
- (9) Hou, T.; Greenlief, C. M.; Keller, S. W.; Nelen, L.; Kauffman, J. F. *Chem. Mater.* **1997**, *9*, 3181.
- (10) Li, Z. S.; Cai, W. Z.; Su, R. Z.; Dong, G. S.; Huang, D. M.; Ding, X. M.; Hou, X. Y.; Wang, X. *Appl. Phys. Lett.* **1994**, *64*, 3425.
- (11) Anderson, G. W.; Hanf, M. C.; Norton, P. R. *Phys. Rev. Lett.* **1995**, *74*, 2764.
- (12) Anderson, G. W.; Hanf, M. C.; Qin, X. R.; Norton, P. R.; Myrtle, K.; Heinrich, B. *Surf. Sci.* **1996**, *346*, 145.
- (13) Liu, C. S.; Kauffman, J. F. *Appl. Phys. Lett.* **1995**, *66*, 3504.
- (14) Sa, S. H.; Kang, M. G.; Park, H. H.; Suh, K. S. *Surf. Coat. Technol.* **1998**, *100–101*, 234.
- (15) Szuber, J.; Bergignat, E.; Hollinger, G.; Polakowska, A.; Koscielniak, P. *Vacuum* **2002**, *67*, 53.
- (16) Yablonovitch, E.; Gmitter, T. J.; Bagley, B. G. *Appl. Phys. Lett.* **1990**, *57*, 2241.
- (17) Lunt, S. R.; Ryba, G. N.; Santangelo, P. G.; Lewis, N. S. *J. Appl. Phys.* **1991**, *70*, 7449.
- (18) Rao, V. J. *Appl. Phys. Lett.* **1989**, *54*, 1799.
- (19) Manorama, V.; Bhorkar, S. V.; Rao, V. J.; Kshirsagar, S. T. *Appl. Phys. Lett.* **1989**, *55*, 1641.
- (20) Bhide, R. S.; Bhorkar, S. V.; Rao, V. J. *J. Appl. Phys.* **1992**, *72*, 1464.
- (21) Shi, F. F. *Surf. Coat. Technol.* **1996**, *82*, 1.
- (22) Mackie, N. M.; Castner, D. G.; Fisher, E. R. *Langmuir* **1998**, *14*, 1227.
- (23) Butoi, C. I.; Mackie, N. M.; Gamble, L. J.; Castner, D. G.; Barnd, J.; Miller, A. M.; Fisher, E. R. *Chem. Mater.* **2000**, *12*, 2014.
- (24) Teare, D. O. H.; Spanos, C. G.; Ridley, P.; Kinmond, E. J.; Roucoules, V.; Badyal, J. P. S. *Chem. Mater.* **2002**, *14*, 4566.
- (25) Lau, K. K. S.; Gleason, K. K. *J. Phys. Chem. B* **1998**, *102*, 5977.
- (26) Lewis, H. G. P.; Edell, D. J.; Gleason, K. K. *Chem. Mater.* **2000**, *12*, 3488.
- (27) Kuhn, G.; Retzko, I.; Lippitz, A.; Unger, W.; Friedrich, J. *Surf. Coat. Technol.* **2001**, *142–144*, 494.
- (28) Beamson, C.; Briggs, D. *High-Resolution XPS of Organic Polymers, The Scienta ESCA300 Database*; Wiley: New York, 1992; p 278.
- (29) Zhang, Y.; Tan, K. L.; Liaw, B. Y.; Liaw, D. J.; Kang, E. T.; Neoh, K. G. *Langmuir* **2001**, *17*, 2265.
- (30) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: Boston, MA, 1990.
- (31) Inagaki, N. *Plasma Surface Modification and Plasma Polymerization*; Technomic Pub. Co.: Lancaster, PA, 1996.
- (32) Hasegawa, F.; Onomura, M.; Mogi, C.; Nannichi, Y. *Solid-State Electron.* **1988**, *31*, 223.
- (33) Moulder, J. F.; Stickle, W. F.; Spol, P. E.; Bomben, K. D. In *X-ray Photoelectron Spectroscopy*; Chastian, J., Ed.; Perkin-Elmer: Eden Prairie, MN, 1992; pp 41 and 95.
- (34) Maier, G. *Prog. Polym. Sci.* **2001**, *26*, 3.
- (35) Castle, J. E. *Surf. Interface Anal.* **1986**, *8*, 137.
- (36) Oshima, M.; Scimeca, T.; Watanabe, Y.; Oigawa, H.; Nannichi, Y. *Jpn. J. Appl. Phys., Part 1* **1993**, *32*, 518.
- (37) Kang, M. G.; Sa, S. H.; Park, H. H.; Suh, K. S.; Oh, K. H. *Thin Solid Films* **1997**, *308–309*, 634.
- (38) Spicer, W. E.; Kendelewicz, T.; Newman, N.; Cao, R.; McCants, C.; Miyano, K.; Lindau, I.; Lillenthal-Weber, Z.; Weber, E. R. *Appl. Surf. Sci.* **1998**, *33–34*, 1009.