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SPECTROSCOPIC INVESTIGATION OF (NH$_4$)$_2$S TREATED GaSeTe FOR RADIATION DETECTOR APPLICATIONS

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Abstract

The surface of the layered III-VI chalcogenide semiconductor GaSeTe was treated with (NH$_4$)$_2$S at 60°C to modify the surface chemistry and determine the effect on transport properties. Room temperature photoluminescence (PL) measurements were used to assess the effect of the (NH$_4$)$_2$S treatment on surface defect states. Evaluation of the subsequent surface chemistry was performed with high-resolution core-level photoemission measurements. Metal overlayers were deposited on the (NH$_4$)$_2$S treated surfaces and the I-V characteristics were measured. The measurements were correlated to understand the effect of (NH$_4$)$_2$S modification of the interfacial electronic structure with the goal of optimizing the metal/GaSeTe interface for radiation detector devices.

The layered III-VI chalcogenide semiconductor GaSeTe has potential for room temperature gamma ray spectroscopy applications due to its 1.77 eV band gap at 300K and high atomic numbers. [1-3] Attempts to fabricate working room temperature radiation detectors using high-resistivity GaSeTe substrates have precipitated the need to engineer the electronic structure of the metal/semiconductor interface. Controlling the oxidation state at this interface will impact the device transport properties and thus an appropriate surface preparation needs to be developed.

Surface passivation of III-V compound semiconductor surfaces is well documented [4] as a means to address the detrimental effects coming from high-density surface states and related Fermi level pinning. Similar surface treatments related to II-VI binary and I-III-VI ternary semiconductor devices have been explored only recently. [5-12] Utilizing cation and anion substitution to cause changes in the surface electronic band structure is an alternative process worth exploring. Specifically, cation substitution causes the conduction band minimum (CBM) to be raised while anion substitution causes the valence band maximum (VBM) to be lowered. [13] Sulfur passivation is another means to affect overall device performance of II-VI or III-VI semiconductors and requires further assessment. [14, 15]

This investigation assessed the effect of $(NH_4)_2S$ on GaSeTe surface composition and electronic structure. $(NH_4)_2S$ was chosen for this investigation because it is a highly reactive sulfur donor and is commonly used for passivating III-V semiconductor surfaces. X-ray photoelectron spectroscopy (XPS) and room temperature photoluminescence (PL) were used to examine the surface reactions associated with the $(NH_4)_2S$ treatment.

GaSe$_x$Te$_{1-x}$ (0.1≤x≤0.9) crystals with resistivities higher than 10^9 Ω cm were grown at EIC by a controlled vertical Bridgman technique using high purity Ga (7N) and in-house zone refined (ZR) precursor materials (Se and Te) to make a homogeneous large grain ingot. The grown ingot was encapsulated in Struers Epofix for metallographic sample preparation. Sequential polishing of the GaSeTe with finer and finer diamond paste followed by colloidal silica resulted in a surface with a mirror finish. Wet chemical treatment of the polished GaSeTe laminar surface was performed using a solution of $(NH_4)_2S$ at 60°C for 10 min. Following treatment, the sample was rinsed in deionized water and blown dry with N_2. XPS was used to investigate the surface chemistry after treatment in an effort to understand the effect of surface composition on room temperature radiation detector performance. Metal contacts for I-V measurements were subsequently applied by electron beam evaporation.

XPS analysis was performed using a focused monochromatic Al Kα x-ray (1486.7 eV) source for excitation and a spherical section analyzer. A 100 μm diameter x-ray beam was used for analysis. The x-ray beam is incident normal to the sample and the x-ray detector is at 45° away from the normal. The pass energy was 23.5 eV giving an energy resolution of 0.3 eV that when combined with the 0.85 eV full width at half maximum (FWHM) Al Kα line width gives a resolvable XPS peak width of 1.2 eV FWHM. Deconvolution of non-resolved peaks was accomplished using Multipak 6.1A (PHI) curve fitting routines. Binding energies were referenced to the C 1s photoelectron line arising from adventitious carbon at 284.8 eV. Low energy electrons were used for specimen neutralization.

XPS survey spectra of the as treated GaSeTe laminar surface was acquired to determine surface stoichiometry and impurity concentrations. The quantitative surface compositional analyses and elemental ratios are summarized in Table I. The $Ga/(Te + Se)$ ratio indicates that the as received laminar surface is slightly Ga-rich and, based on the Ga 2p core-level binding energy at 1118.2 eV, FWHM 1.8 eV, indicates that this excess Ga is bonded as Ga_2O_3. [16, 17] Compositional analysis following the $(NH_4)_2S$ treatment at 60°C for 10 minutes reveals that the Ga concentration at the surface increases and the Ga 2p core level energy decreases to 1118.0 eV, FWHM 1.2 eV. Residual S was also detected on the surface and is certainly a result of the $(NH_4)_2S$ processing although anion substitution is not evident.

The XPS Te 3d core-level spectra for the as received and $(NH_4)_2S$ processed surfaces are presented in Fig. 1. The Te $3d_{5/2}$ spin-orbit component for the as received surface is 572.8 eV with a FWHM of 1.6 eV, and has multiple components representing Te^0 and lattice-bound Te^{2-}. [11, 12, 15] There is also a Te $3d_{5/2}$ spin-orbit component at 576.0 eV indicative of Te^{4+} bound as TeO_2. This peak is absent in spectrum for the $(NH_4)_2S$ processed surface indicating the $(NH_4)_2S$ treatment removes the oxide and results in a stable surface that is passivated to any further oxidation.

The PL spectra presented in Fig. 2 were obtained before and after $(NH_4)_2S$ treatment using a spectrograph (SpectraPro 300i) equipped with a back-thinned LN-cooled CCD camera (Roper Scientific, Spec-10:100B(LN)). The sample was excited using a 633 nm laser excitation (~500 μW). The laser was focused using a high numerical aperture objective (UMPLFL 100X, NA=0.95, Olympus). Spectra were corrected using a luminosity standard (Model 63355, Oriel-Newport, Stratford,

Connecticut). Different areas showed vastly different PL spectra (there are several spectra with peaks between 800-850 nm not shown). The PL peak at 700 nm represents the 1.77 eV bandgap emission at 300K of GaSeTe. The shifted PL peak at 755 nm observed for the $(NH_4)_2S$ treated sample represents 1.64 eV emission (130 meV difference). The mean integrated intensity for the treated sample (6 spectra) was nearly 40% higher than that of the untreated sample (8 spectra). The 130 meV difference in conjunction with changes in intensity may indicate anion substitution by the sulfur and possibly passivation of surface defect states, respectively.

The current vs voltage characteristics of 100 μm diameter Al-$GaSe_{0.5}Te_{0.5}$-Pt diodes with guard rings are shown in Fig. 3. The ammonium sulfide treatment was performed on one of the samples after dicing and polishing prior to diode fabrication. Voltage was applied to the topside aluminum contact in both cases. For the sample with ammonium sulfide treatment the diode appears to be forward biased with positive voltage applied to the Al contact, where as the untreated sample shows the opposite polarity. This possibly indicates a change in the Fermi level pinning at the metal/GaSeTe interface.

The effect of the $(NH4)_2S$ treatments on surface conductivity was studied on the nonlaminar of GaSeTe sample. The nonlaminar surface was prepared using the cutting and polishing procedure described above. Gold electrode patterns were fabricated using standard photolithography and lift off processes. Transmission line method (TLM) patterns were used to evaluate the change in sheet resistance of the material and circular diode patterns were used to measure the change in bulk current after each treatment. [2, 12] Current vs. voltage measurements were performed on the TLM patterns and diodes as fabricated, after 1 minute in H_3PO_4:H_2O (1:10), after 1 minutes in H_2O_2 (30% dilute), a

H_3PO_4:H_2O_2:H_2O (1:1:10) treatment for 5 minutes followed by the $(NH_4)_2S$ for 10 minutes at 60°C. Normalized sheet resistance and diode resistance as measured using TLM patterns and circular diode patterns respectively after various surface treatments are presented in Fig. 4. Similar trends are observed for both measurements, namely after phosphoric acid treatment the effective resistance decreases, possibly due to the removal of a passivating native oxide as was shown in previously using XPS [12]. Following the hydrogen peroxide treatment, a stable surface TeO_x is formed which increases the effective resistance by acting as surface passivation. The $(NH_4)_2S$ treatment is found to increase the sheet resistance significantly, as the sulfur ions passivate surface states.

We have shown that $(NH_4)_2S$ can be used to modify GaSeTe surface chemistry and device transport properties. Results of the high-resolution photoemission measurements on the Ga 2p and Te 3d core lines show that the sulfur treatment has passivated the surface to any further oxidation. Furthermore, the PL peak emission shift and increased intensity after treatment may indicate anion substitution by the sulfur and passivation of surface defect states. The increased sheet resistance noted after treatment provides a pathway forward to reducing surface leakage current and improving device performance.

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Figure Captions

Figure 1.   XPS Te 3d spectra for the as received and $(NH_4)_2S$ processed GaSeTe.

Figure 2.   Room temperature photoluminescence measurements for the GaSeTe before and after $(NH_4)_2S$ treatment.

Figure 3.   Current vs voltage characteristics of 100 μm diameter Al-GaSe$_{0.5}$Te$_{0.5}$-Pt diodes with guard rings before and after $(NH_4)_2S$ treatment.

Figure 4.   Normalized sheet resistance and diode resistance as measured using TLM patterns and circular diode patters respectively after various surface treatments.

Table I. Relative XPS Surface Compositional Analysis (atomic %) of the $(NH_4)_2S$ treated GaSeTe

Sample	Ga	Te	Se	S	O	Ga/(Te + Se) ratio
as received	17.5	4.8	7.2	–	70.5	1.45
10 min $(NH_4)_2S$	62.0	21.2	14.0	1.8	–	1.76