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Spectroscopic investigation of $(NH_4)_2S$ treated GaSeTe for radiation detector applications

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ABSTRACT

The surface of the layered III–VI chalcogenide semiconductor GaSeTe was treated with $(NH_4)_2S$ at 60 °C to modify the surface chemistry and determine the effect on transport properties. X-ray photoelectron spectroscopy and room temperature photoluminescence were used to examine the surface reactions and effect on surface defect states of the $(NH_4)_2S$ treatment. Metal overlayers were deposited on the $(NH_4)_2S$ treated surfaces and the I–V characteristics were measured. The measurements were correlated to understand the effect of $(NH_4)_2S$ modification of the interfacial electronic structure with the goal of optimizing the metal/GaSeTe interface for radiation detector devices.

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1. Introduction

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 300 K and high atomic numbers [1–3]. Since GaSeTe is a highly anisotropic material 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 [5–9]. Utilizing anion substitution to cause changes in the surface electronic band structure is an alternative process worth exploring. Specifically, sulfur passivation is a means to affect overall device performance of II–VI or III–VI semiconductors and requires further evaluation [10,11]. This paper assesses the effect of $(NH_4)_2S$, a highly reactive sulfur (anion) donor, on GaSeTe surface composition and correlates the results with transport properties.

2. Experimental

$GaSe_xTe_{1-x}$ $(0.1 \le x \le 0.9)$ crystals with resistivities higher than 10^9 Ω cm were grown at EIC by a controlled vertical Bridgman technique using high purity Ga (7 N) and in-house zone refined (ZR) precursor materials (Se and Te) to make a homogeneous large grain ingot. Sequential polishing of the GaSeTe laminar (cleaved) surface with finer and finer diamond paste followed by colloidal silica resulted in a surface with a mirror finish. This surface was treated using a solution of $(NH_4)_2S$ at 60 °C for 10 min, then rinsed in deionized water and blown dry with N_2. X-ray photoelectron spectroscopy (XPS) was used to quantify the surface composition after treatment.

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. The collected data were referenced to an energy scale with binding energies for Cu $2p_{3/2}$ at 932.72 ± 0.05 eV and Au $4f_{7/2}$ at 84.01 ± 0.05 eV. Binding energies were also referenced to the C 1s photoelectron line arising from adventitious carbon at 284.8 eV. Low energy electrons were used for specimen neutralization.

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Table 1
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

3. Results and discussion

XPS survey spectra of the as received and treated GaSeTe laminar surface were acquired to determine surface stoichiometry and impurity concentrations. The quantitative surface compositional analyses and elemental ratios are summarized in Table 1. 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 [12]. Following the $(NH_4)_2S$ treatment at 60 °C for 10 min, 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 laminar 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-} [9,12]. 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 that the $(NH_4)_2S$ treatment completely removes the oxide.

The PL spectra presented in Fig. 2 were obtained before and after $(NH_4)_2S$ treatment using a spectrograph equipped with a back-thinned LN-cooled CCD camera. The sample was excited using a focused 633 nm laser excitation (~500 µW) and spectra were corrected using a luminosity standard (Model 63355, Oriel-Newport). The broad PL peak centered at 700 nm represents the 1.77 eV bandgap emission at 300 K of GaSeTe. The width of this peak and the presence of the emission tail are an indication that this semiconductor has defect states that affect the band edge emission. The shifted PL peak at 755 nm observed for the $(NH_4)_2S$ treated sample represents 1.64 eV emission (130 meV difference) and does not exhibit an emission tail. 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 and peak width may indicate anion substitution by the sulfur and possibly passivation of surface defect states, respectively.

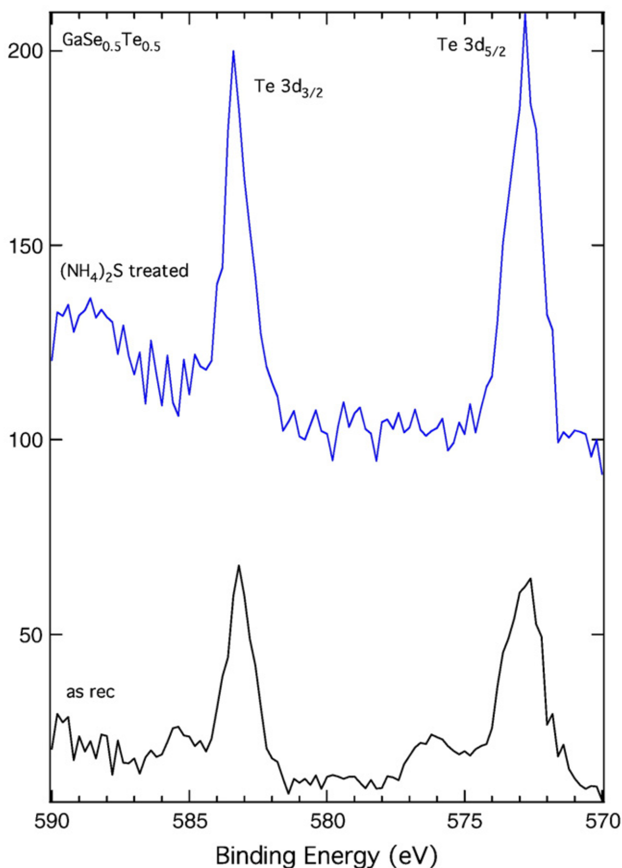

Fig. 1. XPS Te 3d spectra for the as received and $(NH_4)_2S$ processed GaSeTe.

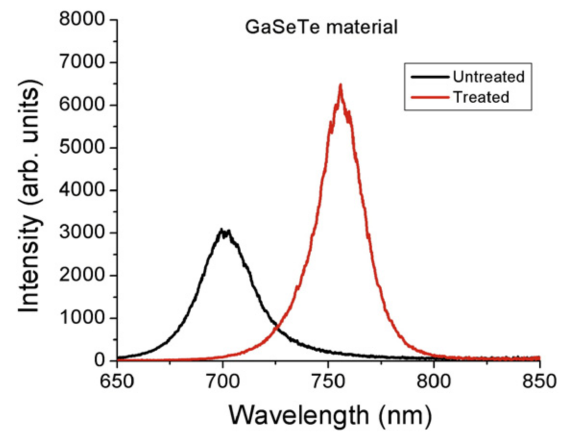

Fig. 2. Room temperature photoluminescence measurements for the GaSeTe before and after $(NH_4)_2S$ treatment.

The effect of the (NH4)$_2$S treatments on surface conductivity was studied on the nonlaminar surface of a $GaSe_{0.5}Te_{0.5}$ sample. The nonlaminar surface was prepared using the cutting and polishing procedure described above as opposed to a cleaved laminar surface. 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 surface current after each treatment [3,9]. Current vs. voltage measurements were performed on the TLM patterns and diodes described above for

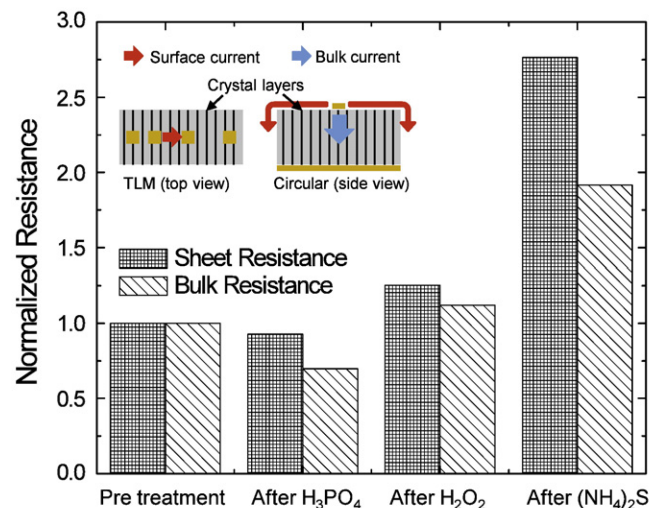

Fig. 3. Normalized sheet resistance and diode resistance as measured using TLM patterns and circular diode patterns respectively after various surface treatments. Inset: schematic diagram of TLM patterns and circular patterns used in surface treatment experiments.

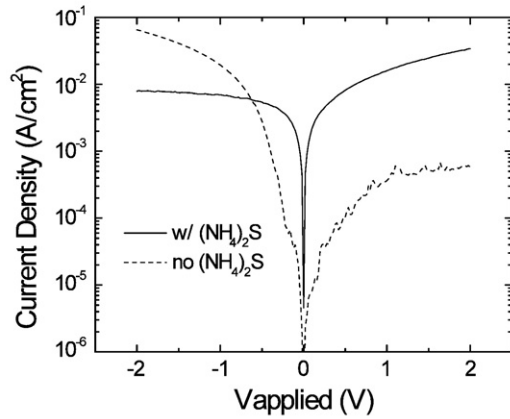

Fig. 4. Current vs voltage characteristics of 100 µm diameter Al–$GaSe_{0.5}Te_{0.5}$–Pt Schottky diodes with guard rings with and without $(NH_4)_2S$ treatment prior to metal deposition.

four cases: as fabricated, after 1 min in H_3PO_4:H_2O (1:10), after 1 min in H_2O_2 (30% dilute), a H_3PO_4:H_2O_2:H_2O (1:1:10) treatment for 5 min followed by the $(NH_4)_2S$ for 10 min at 60 ° C. Normalized sheet resistance and diode resistance measurements are presented in Fig. 3. While the exact crystallographic orientation was not measured, current transport in the TLM pattern is perpendicular to the crystal layers and is a combination of perpendicular to the layers and along the layers for the circular patterns (inset to Fig. 3.) Results show that after phosphoric acid treatment the resistance decreases, possibly due to the removal of a passivating native oxide as was shown previously [9]. Following the hydrogen peroxide treatment, 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 suggesting that the sulfur ions further passivate surface states.

Schottky diodes were also fabricated on the nonlaminar surface of two $GaSe_{0.5}Te_{0.5}$ crystals using Al as the Schottky metal and Pt as the ohmic. The current versus voltage characteristics of 100 µm diameter Al–$GaSe_{0.5}Te_{0.5}$–Pt diodes with guard rings are shown in Fig. 4. $(NH_4)_2S$ treatment for 10 min at 60 °C was performed on one of the samples after dicing and polishing prior to diode fabrication. For the sample with $(NH_4)_2S$ treatment the diode appears to be forward biased with positive voltage applied to the Al contact, whereas the untreated sample shows the opposite polarity. This possibly indicates a change in the Fermi level pinning at the metal/GaSeTe interface leading to a lower Schottky barrier, as indicated by the increased reverse bias leakage current and lower turn on voltage.

4. Conclusions

We have shown that $(NH_4)_2S$ can be used to modify GaSeTe surface chemistry and device transport properties. Results of the XPS measurements indicate that the sulfur treatment has stabilized the surface. 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 reduce surface leakage current and improve device performance.

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