

# **X-Ray Photoelectron Spectroscopy of Transition Metal Doped Gallium Sesquiselenide**

Paula Lampen

University of Washington REU Program 2008

Marjorie Olmstead, Advisor

The chemical environment, structural features, and resilience of manganese and chromium doped heteroepitaxial gallium sesquiselenide ( $\text{Ga}_2\text{Se}_3$ ) on an arsenic-terminated silicon substrate are explored using X-Ray Photoelectron Spectroscopy (XPS).

## *Introduction*

The Chalcogenides group at the University of Washington is currently investigating the growth and properties of semiconducting chalcogenides—materials whose interesting structural, electronic, and optical properties may be compatible with silicon nanotechnologies. Silicon has long been predicted to be an ideal semiconductor for spintronic applications but this potential has remained untapped as an impedance-matched room temperature ferromagnet with spin-preserving transport through a silicon interface has yet to be discovered. The group is focusing on the candidate material  $\text{Ga}_2\text{Se}_3$ .

$\text{Ga}_2\text{Se}_3$  is a dilute magnetic semiconductor with intrinsic vacancies that have been shown to spontaneously order upon growth on  $\text{Si}(001):\text{As}$ , forming nanoscale ridges several tens of nm long, and about 1 nm wide.<sup>1</sup> XPS of samples of transition metal (TM) doped  $\text{Ga}_2\text{Se}_3$  was performed at the Advanced Light Source (ALS), where low energy x-rays allowed the characterization of the surface to a depth of 0.5nm, probing only the tops of the surface islands. The new PHI Versaprobe XPS system at the University of Washington uses a higher energy x-ray beam that can generate a signal 2 nm deep into the material, thus seeing the “whole islands”. The goal of this project was to characterize the composition of the same films of TM: $\text{Ga}_2\text{Se}_3$  at this greater depth and after lengthy exposure to air.

## *Principles of the Technique*

XPS is a surface analysis technique based on the photoelectric effect in which a sample is irradiated with monochromatized soft x-rays. Photons of energy  $h\nu$  cause the emission of electrons from core and valence levels of the solid. The kinetic energy of the resulting photoelectrons is given by  $\text{KE} = h\nu - \text{BE} - \Phi$ , where BE is the binding energy of the electron prior to ionization, and  $\Phi$  is the work function of the material being probed. Electrons escaping the surface are collected and sorted by an energy analyzer.

The XPS system utilized for this project contains a hemispherical energy analyzer. An electric field is applied between two concentric spherical surfaces. The radius of the path traveled by an incoming photoelectron is proportional to its kinetic energy, and electrons of differing energies become dispersed spatially at the far end of the analyzer. The number of electrons at each energy interval is recorded, and an energy spectrum is constructed.

Only photoionized electrons originating within a few angstroms of the surface escape without loss, forming sharp energy peaks against the background. These photoelectron lines are due to the ionization of core-level electrons in the emitting atoms, and are often the most

prominent features on the spectrum. The characteristic set of core-level binding energies possessed by each element gives rise to photoelectrons of specific energies for a given photon energy. Elemental identification of a sample is a relatively simple task as the characteristic spectra of individual elements are well-established, and readily available in the literature.<sup>2</sup> With quantum mechanically calculated photoionization cross sections for various core levels, peak areas and intensities can be converted to atomic concentrations to determine the percent composition of a sample.

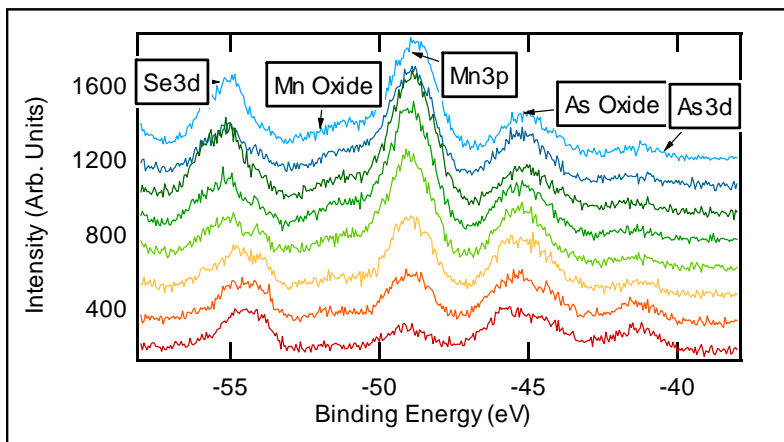
Although elemental and concentration information can be obtained from XPS, the most valuable application of this tool is in chemical environment analysis. Bonding with other atoms causes a change in the electrostatic screening of the core electrons when the valence electrons are attracted or repulsed in the atom.<sup>3</sup> Consequently, these changes in the local electronic environment alter the original binding energy of the electrons. This manifests as a shift in the photoelectron peak on the energy spectrum.

### Procedure

As a material with potential for wide use in device applications, the consequences of ageing and exposure to various common contaminants on TM:Ga<sub>2</sub>Se<sub>3</sub> are of interest. The films examined during this project were Mn:Ga<sub>2</sub>Se<sub>3</sub> and Cr:Ga<sub>2</sub>Se<sub>3</sub>, grown *in situ* via molecular beam epitaxy at the ALS approximately one year prior by other group members. Like other surface sensitive techniques, XPS is performed under Ultra High Vacuum conditions (ambient pressures of less than 10<sup>-9</sup> Torr), as even slight contamination can alter the results. However, the films had been exposed to atmosphere since their removal from the ALS.

Survey scans and detailed spectra were collected for each of these samples with 0.1eV resolution on simple peaks, and 0.05eV resolution on peaks that exhibited more complex structure. The data were then exported to the software program Igor where curves were fit to Voigt, spin-orbit Voigt, and Gaussian functions. This software allows the user to determine exact peak locations, areas, and intensities; this ability is especially valuable for determining small peak shifts and identifying overlapping peaks.

As expected from a sample exposed to atmosphere, oxygen, carbon, and nitrogen peaks were observed in addition to gallium, selenium, manganese, silicon, and arsenic. In addition to its elemental core peaks and Auger lines, the presence of oxygen is evidenced by peaks that occur a few tenths of an eV to several eV higher in binding energy than the elemental lines as



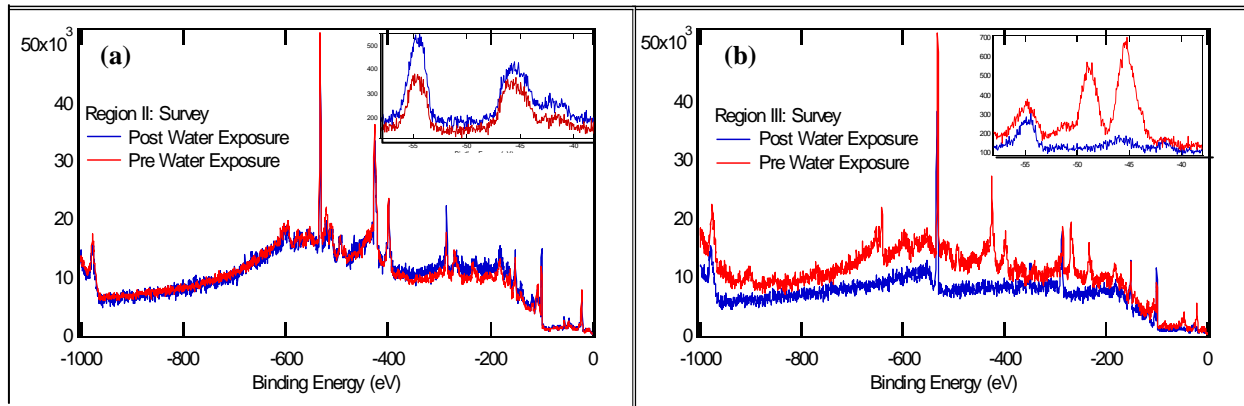
**Fig. 1** The 35eV to 60eV binding energy window of a Ga<sub>2</sub>Se<sub>3</sub> film with a Mn gradient. Spectra were collected 1mm apart along the sample with 0.1eV resolution, and are offset for clarity. Mn intensity increases along the sample as expected. Se and As elemental peaks are also visible.

oxides of the elements form. Fig 1 shows spectra of a certain energy range collected at eight successive points 1mm apart across a Ga<sub>2</sub>Se<sub>3</sub> film with manganese concentration varying uniformly across the sample from zero to ten percent. The manganese and arsenic oxide peaks are distinct, and appear quite uniform throughout the film. The selenium peak, however, shifts 1.1eV higher in binding energy as the gradient from low to high manganese concentration is traversed. That the peak shifts towards higher binding energies rather than lower is a telltale sign that the selenium is becoming increasingly oxidized, and not forming a manganese-selenide compound. Thus the presence of manganese appears to enhance the reactivity of selenium, although the reason for this is unknown; this idea warrants further investigation at a later time.

The oxide peaks were in many cases dwarfed by their associated elemental peaks suggesting that the films largely retained their original composition. Additionally, the structural features observed previously on these and similar films were still in evidence. For example, fitting the Se3d peak to spin-orbit Voigt functions reveals two separate chemical environments for Se atoms, separated by about 0.95eV in binding energy. The resulting “double-shouldered” shape has been previously reported<sup>1</sup>.

### *Exposure to Liquids*

To further investigate the resilience of the films, sections of a pure Ga<sub>2</sub>Se<sub>3</sub> film were exposed to de-ionized water or acetone for approximately thirty seconds. For both liquids, although the intensities of individual peaks varied somewhat from the original data, no dramatic chemical shifts occurred, and the spectra retained all the features of the original film (Fig 2a). However, exposure of a 10% manganese-doped film to water caused much of the film to completely dissolve. Fig 2b shows that although traces of selenium and arsenic are still visible, the resulting spectrum closely resembles that of a bare silicon wafer. The disappearance of the films can be attributed to the formation of a particularly soluble manganese-oxide compound. As the most soluble of the oxides, Mn<sub>2</sub>O<sub>7</sub> is a likely candidate.



**Fig.2** (a) Survey spectra from 0 to 1000eV binding energy of a pure Ga<sub>2</sub>Se<sub>3</sub> sample. The pre water exposure data are in red, and the post water exposure data are in blue. The spectrum appears relatively unchanged after exposure to water. Part (b) shows the results of exposing a Mn: Ga<sub>2</sub>Se<sub>3</sub> sample to water. Only oxygen, silicon, carbon and selenium remain in any significant quantities.

It has been proposed that Ga<sub>2</sub>Se<sub>3</sub> films be immersed in a solvent in which TiO<sub>2</sub> nanorods are dissolved in hopes that as the solvent evaporated, the rods would come to rest between the nanoridges formed on the surface of Ga<sub>2</sub>Se<sub>3</sub> and TM:Ga<sub>2</sub>Se<sub>3</sub>. This project reveals that water would be an acceptable solvent in the case of pure Ga<sub>2</sub>Se<sub>3</sub>, but not for transition metal doped films. The violent reaction in the films with manganese also indicates that the effects of water vapor in the air reacting with manganese should be considered as air-exposed Mn:Ga<sub>2</sub>Se<sub>3</sub> films are examined.

### *System Expansion and Future Work*

Although results have indicated that Ga<sub>2</sub>Se<sub>3</sub> is a relatively robust compound, exposure to atmosphere as the samples are moved from one location to another results in the formation of undesired oxides on the surface of the films. With future work in mind, designs have been made to expand the PHI XPS system to include additional chambers for *in situ* growth as well several other surface analysis techniques.

Although a great deal of data was collected over the summer, because of time constraints much of it exists only in raw graphical form. I plan to continue my work on these films in the upcoming months, first completing the Igor fitting of the curves before performing a more rigorous and quantitative analysis of the films.

### *Acknowledgements*

I wish to thank my advisor, Dr. Marjorie Olmstead, along with Dr. Fumio Ohuchi, Tracy Lovejoy, Christina Polwarth, and Esmeralda Yitamben for their invaluable guidance and assistance on this project.

---

<sup>1</sup> Taisuke Ohta *et al.* "Intrinsic Vacancy-Induced Nanoscale Wire Structure in Heteroepitaxial Ga<sub>2</sub>Se<sub>3</sub>/Si(001)". *Phys. Rev. Lett.* 94, (2005).

<sup>2</sup> John F. Moulder *et al.* *Handbook of X-ray Photoelectron Spectroscopy*. (ULVAC-PHI; Enzo, Japan) 1992.

<sup>3</sup> Antonella Rossi *et al.* "XPS Surface Analysis: imaging and spectroscopy of metal and polymer surfaces". Spectroscopy Europe on the World Wide Web at [http://www.spectroscopyeurope.com/Surface\\_16\\_6.pdf](http://www.spectroscopyeurope.com/Surface_16_6.pdf).