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In Applied Chemistry

Studies of specifically modified semiconductor surfaces by means of spectroscopic methods

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Declaration

I hereby certify that the below mentioned work has been written by me and that no other sources except the ones cited below have been used to complete this dissertation.

Place, Date

Signature

Preface:

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List of Abbreviations

UHV	ultra high vacuum
XPS	x-ray photoelectron spectroscopy
PL	Photoluminescence
E_v	energy level of valence band
E_c	energy level of conduction band
E_g	energy level of band gap
E_B	binding energy
E_i	intrinsic Fermi level
THF	Tetrahydrofuran
CAS number	unique numerical identifiers assigned by the Chemical Abstracts Service
R-phrases	Risk Phrases
S-phrases	Safety Phrases
pK_a	logarithmic measure of the acid dissociation constant
IUPAC	International Union of Pure and Applied Chemistry chemical nomenclature
CCD	charge-coupled devices
ESCA	Electron Spectroscopy for Chemical Analysis
E_{photon}	energy of the X-ray photons
$E_{binding}$	binding energy of the electron
$E_{kinetic}$	kinetic energy of the electron as measured by the instrument

Φ	work function of the spectrometer
e.g.	exempli gratia
aq	aqueous
DI	deionized

Abstract

This bachelor thesis focuses on the studies of specifically modified semiconductor surfaces by means of spectroscopic methods. Indium arsenide and gallium arsenide were selected as substrates. After different treatments with sulfide solutions, the substrates were measured by photoluminescence spectroscopy and x-ray photoelectron spectroscopy.

The first part of the thesis describes the general theory related to this work. For example, the band theory of solid and band gap, both are the basic knowledge of semiconductors. Electron binding energy is extremely important for photoelectron spectroscopy.

In the second part of the thesis, general information and properties of the chemicals and substrates being used in this work are shown, which are meaningful of planning and preparing for the experiments and in terms of safety.

The next parts are the descriptions of experimental setups (photoluminescence spectroscopy and x-ray photoelectron spectroscopy) and preparations of the experiments such as prepare of chemical solutions and handle of substrates.

The last part is based on the experimental results. After the implementation of experiments, interpretation and analysis of spectra are described. Further discussion and reasonable conjecture are also written at the end of the thesis.

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1. Introduction

The advances in modern electronic devices are determined by a steady miniaturization of their sizes toward the nanoscale, which enables the increase of device density on a very small footprint. They are based on semiconductor materials which have the unique property to exhibit an electrical conductivity between that of a conductor and an insulator.

This property is based on a band gap between the valence band and the conduction band, so that an electron can jump from the valence band to the conduction band and vice versa [1]. Temperature makes it possible to offer such a little extra energy and induces the electron to jump to the conduction band therefore creating a hole in the valence band. Beside temperature also doping can increase the conductivity of a semiconductor to a large extent, allowing for a tailoring of conductive properties.

In contrast to silicon, which is the basic material used in the integrated circuit [2], and germanium, the semiconductor used for the first transistors [3], there are a number semiconductors which have a high conductivity due to their small band gaps. That makes them interesting for the improvement of device conductivity and for the reduction in the energy consumption of the devices.

Basically the standard used semiconductors appear in column IV of the Periodic Table of Elements or are a combination of elements in columns at equal distance of Column IV on each side [4]. Gallium arsenide (GaAs) and indium arsenide (InAs) which we use in this work are very common compounds, gallium and indium are from column III and arsenic comes from Column V. The semiconductors mentioned above exhibit a direct band gap which means, that a carrier can be levitated from the valence band to the conduction band by photon excitation.

With respect to applications, devices also can become faster if their size is reduced due to the shorter distances carriers need to travel. Therefore extensive research is underway to miniaturize devices. However, the smaller the scale of the material is, the more the material properties are governed by their surface in addition to their volume properties since the surface to volume ratio becomes huge.

Semiconductor surfaces are often non-ideal, featuring complex surface reconstructions and an abundance of dangling bonds. The latter produce localized energy levels in the surface band structure that can act as metastable trapping sites [5].

Because of the termination of a bulk crystal, surface atoms have fewer neighbors than bulk atoms and some chemical bonds are broken at the surface [6], so-called dangling bonds.

The properties of atoms or ions which create the surface are obviously different compared to those of the bulk. Many macroscopic effects of surfaces are due to the change in chemical bonding in electronic structure [6], for example, the surface free energy, the adhesion forces, and the specific chemical reactivity of a particular surface.

Therefore, understanding the properties of the surfaces of solids and the interactions of atoms and molecules with surfaces has been of extreme importance both from technological and from academic points of view and in future will also determine the advances in nanoelectronics.

Surface science is strongly dependent on ultra high vacuum (UHV) technology. It allows the microscopic characterization of surface systems. The way how atoms move to reduce the energy of their surfaces, the amount of layers of atoms involved in this reduction, the electronic and vibration states that are due to this movement, and the final symmetry of the surface layer are all most important in achieving a fundamental and microscopic understanding of the nature of clean surfaces, chemisorptions processes, and the initial stages of interface formation [7].

The dangling bonds of the surface atoms can interact with molecules from the air to form chemisorbed molecules. This leads to the consequence that the electrical properties of the semiconductor change with time. To determine such an effect, surface modification experiments were carried out.

The modification was to first remove oxides and impurities from the surface and then to simultaneously selectively cover the surface with compounds protecting it from the further influence of air. This process is called passivation. It is of interest, how stable this passivation is with time and if it can be removed in ultra high vacuum, so that clean surfaces can be studied.

From an electronic standpoint, passivation should reduce the density of surface states and the velocity of non-radiative surface recombination [8]. This thesis deals with a comparative investigation of 3 different treatments to the semiconductors surfaces InAs and GaAs. An assessment of the effect on surface composition and on surface states for all three treatments is to be made.

X-ray photoelectron spectroscopy has been used extensively to investigate clean surfaces of III-V compounds prepared in different ways. To examine the benefits of the sulfide passivation approach for InAs surfaces, we use XPS to characterize the initial composition of passivated surfaces and their stability in air and UHV. Such measurements were carried out using a high-resolution spectrometer with a monochromatized Al *K*α source.

Also we use steady-state photoluminescence method to probe the electrical recombination properties of various GaAs surfaces. In general, the changes in steady-state PL intensity show the effect of sulfide passivation.

2. General Theory

2.1 Band Theory of Solid

Band theory, in solid-state physics, is a theoretical model describing the states of electrons, in solid materials, that can have values of energy only within certain specific ranges [9]. How an electron behaves in a solid (and hence its energy) is related to the behavior of all other particles around it.

A useful way to visualize the difference between conductors, insulators and semiconductors is to plot the available energies for electrons in the materials. Instead of having discrete energies as in the case of free atoms, the available energy states form bands. Crucial to the conduction process is whether or not there are electrons in the conduction band.

In insulators the electrons fill states in the valence band which are separated by a large gap from the conduction band, in conductors such as metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap for the carriers. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically [10].

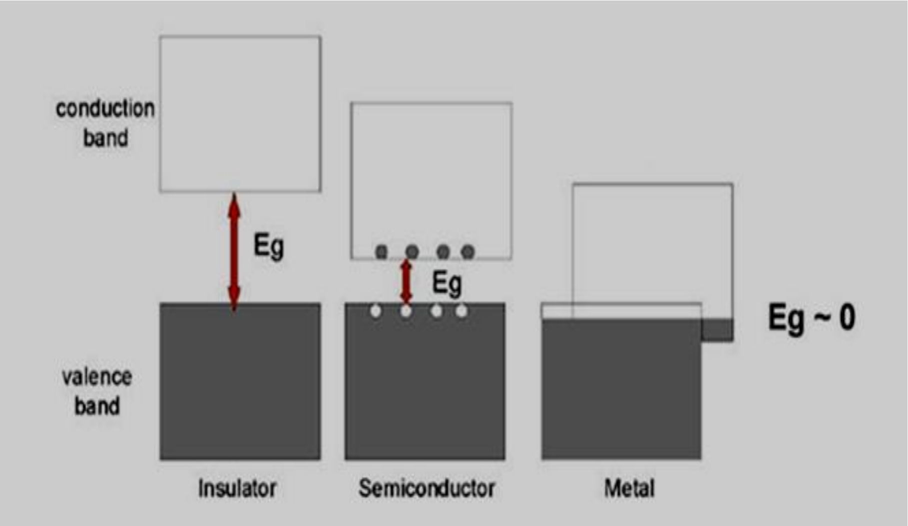


Figure 1. Band theory of solid, schematic band diagrams for an insulator, a semiconductor, and a metal.

For intrinsic semiconductors such as silicon and germanium, the Fermi level is essentially halfway between the valence and conduction bands. Although no conduction occurs at 0 K, at higher temperatures a finite number of electrons can reach the conduction band and provide some current. In doped semiconductors, extra energy levels are added [11].

2.2 Band gap

In solid-state physics, a band gap, also called an energy gap or bandgap, is an energy range in a solid where no electron states can exist [12]. In graphs of the electronic band structure of insulating and semiconducting solids, the band gap generally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band.

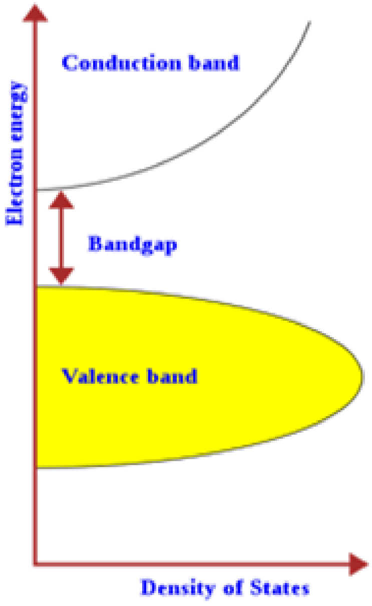


Figure 2. Diagram of relationship between conduction band, valence band and band gap

This is equivalent to the energy required to free an outer shell electron from its orbit around the nucleus to become a mobile charge carrier, able to move freely within the solid material.

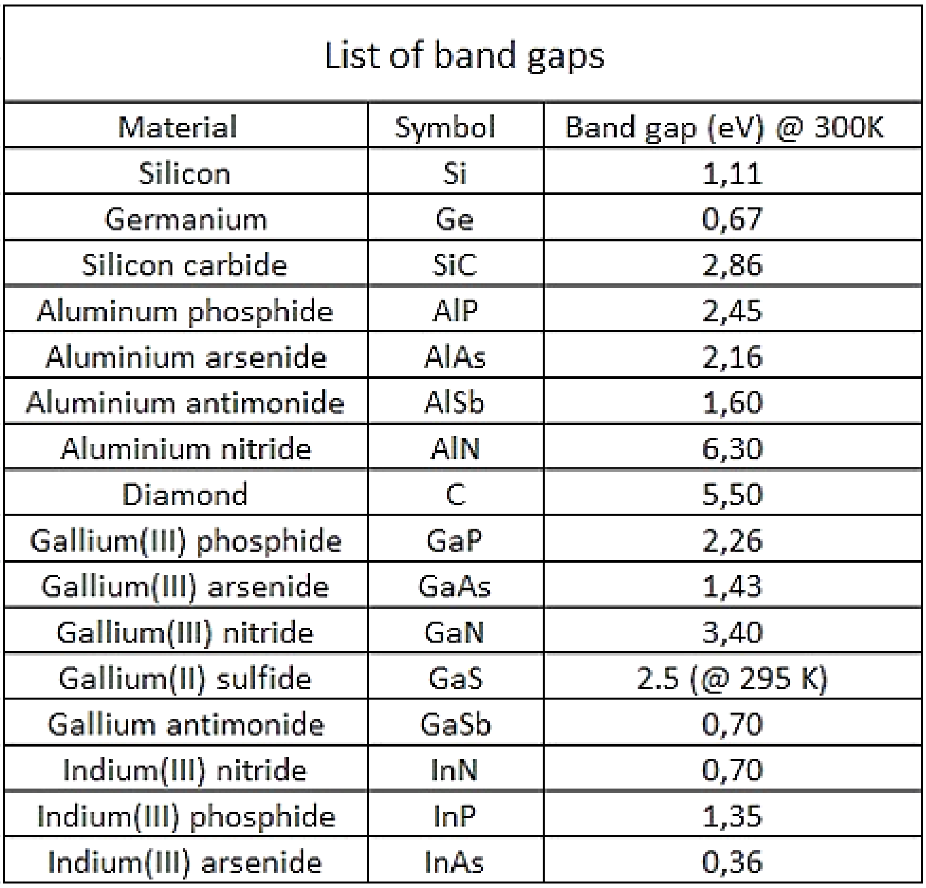
Therefore the band gap is a major factor determining the electrical conductivity of a solid [13].

A semiconductor is a material with a small but non-zero band gap that behaves as an insulator at absolute zero but allows thermal excitation of electrons into its conduction band at temperatures that are below its melting point. In contrast, a material with a large band gap is an insulator. In conductors, the valence and conduction bands may overlap, so they may not have a band gap [14].

The band structure of a semiconductor gives the energy of the electrons on the y-axis and is called a "band diagram". The lower energy level of a semiconductor is called the "valence band" (E_V) and the energy level at which an electron can be considered free is called the "conduction band" (E_C). The band gap (E_g) is the gap in energy between the bound state and the Free State, between the valence band and conduction band. Therefore, the band gap energy is the minimum change in energy required to excite the electron so that it can participate in conduction.

Once the electron becomes excited into the conduction band, it is free to move about the semiconductor and participate in conduction. However, the excitation of an electron to the conduction band will also allow an additional conduction process to take place. The excitation of an electron to the conduction band leaves behind an empty space for an electron. An electron from a neighboring atom can move into this empty space. When this electron moves, it leaves behind another space. The continual movement of the space for an electron, called a "hole", can be illustrated as the movement of a positively charged particle through the crystal structure. Consequently, the excitation of an electron into the conduction band results in not only an electron in the conduction band but also a hole in the valence band. Thus, both the electron and hole can participate in conduction and are called "carriers" [15].

The band-gap energy of semiconductors tends to decrease with increasing temperature. When under a higher temperature, the amplitude of atomic vibrations increases, and thus leads to larger interatomic space.



List of band gaps		
Material	Symbol	Band gap (eV) @ 300K
Silicon	Si	1,11
Germanium	Ge	0,67
Silicon carbide	SiC	2,86
Aluminum phosphide	AlP	2,45
Aluminium arsenide	AlAs	2,16
Aluminium antimonide	AlSb	1,60
Aluminium nitride	AlN	6,30
Diamond	C	5,50
Gallium(III) phosphide	GaP	2,26
Gallium(III) arsenide	GaAs	1,43
Gallium(III) nitride	GaN	3,40
Gallium(II) sulfide	GaS	2.5 (@ 295 K)
Gallium antimonide	GaSb	0,70
Indium(III) nitride	InN	0,70
Indium(III) phosphide	InP	1,35
Indium(III) arsenide	InAs	0,36

Table 1. List of common band gaps

2.3 Electron Binding Energy

The electron binding energy of an atom or molecule, referred to as the ionization energy, describes the minimum amount of energy required to remove an electron (to infinity) from the atom or molecule into the gaseous state [16].

$$X + \text{Energy} \rightarrow X^{+} + e^{-} \qquad \text{(eq.1)}$$

A negatively charged electron is attracted to the nucleus of an atom which is positively charged there. The amount of energy required to be pull an electron away from the attractive (Coulombic) force is called the binding energy.

For all atoms beside the hydrogen atom, more than one electron is present in an orbit around a nucleus. Electrostatic repulsion must also be considered which arises between the electrons. Because of this additional repulsion, a smaller energy is sufficient to remove an electron from the nucleus. This electron-electron repulsion makes the problem unsolvable analytically. However, many effective and accurate numerical methods have been developed to calculate the binding energies including these additional terms.

The most basic description of the electrons around an atom is in terms of their orbital angular momentum. This gives rise to the commonly known labels 1s, 2s, 2p, etc. The next most important term is that of the spin-orbit interaction and splits all of the non-s electrons into two different levels, for instance, 2p (1/2) and 2p (3/2). The splitting becomes very large for the heavy atoms so that the use of these same labels is no longer accurate. Nevertheless, it is possible to identify each electron with this type of label. The spin-orbit splitting is averaged for each spin-orbit pair, accounting for the different degeneracies of the two states.

Therefore the binding energies that are reported are what would be expected considering only Coulombic electrostatic forces and is what might be observed in a spectrometer with very poor resolution [17]. The binding energies of electrons of an element and its bonding partner are characteristic for the respective bond and can therefore be used to identify surface composition XPS.

The n^{th} ionization energy refers to the amount of energy required to remove an electron from the species with a charge of (n-1). For example, the first three ionization energies are defined as follows:

1st ionization energy

$$X \rightarrow X^{+} + e^{-} \quad \text{(eq.2)}$$

2nd ionization energy

$$X^{+} \rightarrow X^{2+} + e^{-} \quad \text{(eq.3)}$$

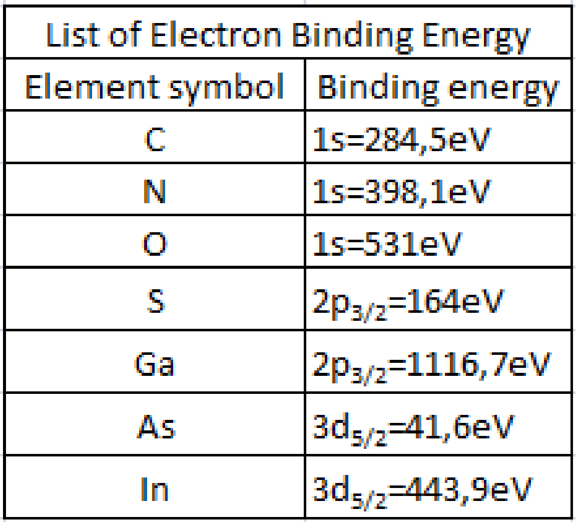
3rd ionization energy

$$X^{2+} \rightarrow X^{3+} + e^{-} \quad \text{(eq.4)}$$

It has sometimes proven useful to consider the effect that the other electrons have upon a given electron as if they "stood in the way" between it and the nucleus to which it was attracted. This effect would be to diminish the effective nuclear charge by "shielding" the actual nuclear charge from the electron.

The units for ionization energy vary from discipline to discipline. In physics, the ionization energy is typically specified in electron volts (eV) and refers to the energy required to remove a single electron from a single atom or molecule. In chemistry, the ionization energy is typically specified as a molar quantity (molar ionization energy or enthalpy) and is reported in units of kJ/mol or kcal/mol (the amount of energy it takes for all the atoms in a mole to lose one electron each).

Reported here are the best values for the binding energy of atoms which are related to the following experiments.



List of Electron Binding Energy	
Element symbol	Binding energy
C	1s=284,5eV
N	1s=398,1eV
O	1s=531eV
S	$2p_{3/2}$=164eV
Ga	$2p_{3/2}$=1116,7eV
As	$3d_{5/2}$=41,6eV
In	$3d_{5/2}$=443,9eV

Table 2. List of electron binding energy related in this work

2.4 Semiconductor doping

The process of intentionally adding impurities to a semiconductor is known as doping. The doping of semiconductors has a dramatic effect on their electrical conductivity and is the basis for solid state electronics.

The conductivity of semiconductors may easily be modified by introducing impurities, which are also called dopants - into their crystal lattice. The dopant concentration added to a pure semiconductor varies its level of conductivity. The conductivity of doped semiconductors is referred to as extrinsic while that of the pure semiconductors are referred as intrinsic. By such a doping process, the electrical conductivity may be changed by many orders of magnitude.

The effects of semiconductor doping were long known empirically in such devices as crystal radio detectors and selenium rectifiers. However, the process was formally first developed by John Robert Woodyard working at Sperry Gyroscope Company during World War II [18]. The demands of his work on radars denied Woodyard the opportunity to pursue research on semiconductor doping. However, after the war ended, his patent proved the grounds of extensive litigation by Sperry Rand [19]. Related work was performed at Bell Labs by Gordon K. Teal and Morgan Sparks [20].

A 1 cm^3 specimen of a metal or semiconductor has of the order of 10^{22} atoms. In a metal, every atom donates at least one free electron for conduction, thus 1 cm^3 of metal contains in the order of 10^{22} free electrons, whereas a 1 cm^3 sample of pure germanium at 20 °C contains about 4.2×10^{22} atoms, but only 2.5×10^{13} free electrons and 2.5×10^{13} holes. The addition of 0.001% of arsenic (an impurity) donates an extra 10^{17} free electrons in the same volume and the electrical conductivity is increased by 5 orders of magnitude.

Doping a semiconductor crystal introduces allowed energy states within the band gap but very close to the energy band that corresponds to the dopant type. In other words, donor impurities create states near the conduction band while acceptors create states near the valence band. The gap between these energy states and the nearest energy band is usually referred to as dopant-site bonding energy or E_B and is relatively small. For example, the E_B for boron in silicon bulk is 0.045 eV, compared with silicon's band gap of about 1.12 eV. Because E_B is so small, room temperature is hot enough to thermally ionize practically all of the dopant atoms and create free carriers in the conduction or valence bands.

Dopants also have the important effect of shifting the energy bands relative to the Fermi level. The energy band that corresponds with the dopant with the greatest concentration ends up closer to the Fermi level. Since the Fermi level must remain constant in a system in thermodynamic equilibrium, stacking layers of materials with different properties leads to many useful electrical properties induced by band bending, if the interfaces can be made cleanly enough. For example, the p-n junction's properties are due to the band bending that happens as a result of the necessity to line up the bands in contacting regions of p-type and n-type material. This effect is shown in a band diagram. The band diagram typically indicates the variation in the valence band and conduction band edges versus some spatial dimension, often denoted x. The Fermi level is also usually indicated in the diagram. Sometimes the intrinsic Fermi level, E_i, which is the Fermi level in the absence of doping, is shown. These diagrams are useful in explaining the operation of many kinds of semiconductor devices [21].

The materials chosen as suitable dopants depend on the atomic properties of both the dopant and the material to be doped. In general, dopants that produce the desired controlled changes are classified as either acceptors or donors. Semiconductors doped with donor impurities are called n-type, while those doped with acceptor impurities are known as p-type.

During manufacture, dopants can be diffused into the semiconductor body by contact with gaseous compounds of the desired element, or ion implantation can be used to accurately position the doped regions.

Atoms with one more valence electron than silicon are used to produce "n-type" semiconductor material. These n-type materials are group V elements in the periodic table, and thus their atoms have 5 valence electrons that can form covalent bonds with the 4 valence electrons that silicon atoms have. Because only 4 valence electrons are needed from each atom (silicon and n-type) to form the covalent bonds around the silicon atoms, the extra valence electron present (because n-type materials have 5 valence electrons) when the two atoms bond is free to participate in conduction. Therefore, more electrons are added to the conduction band and hence increase the number of electrons present.

Atoms with one less valence electron result in "p-type" material. These p-type materials are group III elements in the periodic table. Therefore, p-type material has only 3 valence electrons with which to interact with silicon atoms. The net result is a hole, as not enough electrons are present to form the 4 covalent bonds surrounding the atoms. In p-type material, the number of electrons trapped in bonds is higher, thus effectively increasing the number of holes.

2.5 Sulfide Passivation

The surfaces of most III/V semiconductors are notoriously reactive, primarily because they contain large concentrations of dangling bonds on any given crystal plane. Some of these may be terminated by the formation of native oxides, for example, In_xO_y and/or As_xO_y in the case of InA. Gallium arsenide has long been known to have poor surface electronic properties which are attributed to the fact that As_2O_3 [22]is thermodynamically unstable in the presence of GaAs and reacts to form “As”.

In the past years, much effort has been expended to improve the III/V semiconductors surface electronic properties. One of the most effective methods to improve these properties is by treatment in sulfur-containing media, such as H_2S, Na_2S [23] [24] [25] [26], $(NH_4)_2S$ [24], and $(NH_4)_2S_x$ [27] [28] [29] solutions.

Chemically, the purpose of passivation is to remove the native oxide layer and to form a thin protective coating on the semiconductor surface which would inhibit oxidation in the atmosphere. From the electronic characteristics point of view, passivation should reduce the density of surface states and the velocity of non-radiative surface recombination.

In contrast to other methods of surface passivation, the sulfide technique, which consists in treating the semiconductor with aqueous sulfide solutions, combines chemical with electronic passivation [30]. On the one hand, this method permits the removal of the oxide layer from the semiconductor surface and the formation of a thin practically monatomic sulfide coating on it. On the other hand, sulfide passivation results in a noticeable decrease of the surface-state density and of the surface recombination velocity, thus permitting improvement of the performance of some semiconductor devices.

Most of the earlier chemical passivation studies were performed on bulk GaAs using sodium and ammonium sulfide based solutions such as $Na_2S\cdot 9H_2O$ and $(NH_4)_2S$.It has been reported that the Schottky barrier heights of the diodes formed on the $(NH_4)_2S_x$ -treated GaAs are strongly dependent on the metal work function [31], which suggests that the $(NH_4)_2S_x$ treatment can effectively reduce the surface state density. A model has been proposed [32] to explain the difference in the treatment effect among those sulfides mentioned above, in which Ga-S bonds were assumed to play the most important role.

However, Sandroff et al. reported that only As-S bonds were observed under their experimental conditions. Although Spindt et al. [33] found that Ga-S bonds exist on the $(NH_4)_2S_x$-treated GaAs, no information on the core levels of the S atoms has been reported.

In this work three different sulfide solutions Na_2S, $(NH_4)_2S$ and $(NH_4)_2S_x$ will be used to do the passivation of gallium arsenide and indium arsenide surfaces. Similar studies recently performed on InAs suggested that improved InAs surface properties may also be realized by chemical treatment of the material with aqueous Na_2S, $(NH_4)_2S$ or $(NH_4)_2S_x$ solutions like gallium arsenide.

3. Chemicals and Substrates

3.1 Chemicals

3.1.1 Sodium sulfide

Sodium sulfide is the chemical compound with the formula Na_2S, or more commonly its hydrate $Na_2S \cdot 9H_2O$. Both sodium sulfide and its hydrate are colorless water-soluble salts. Their solutions are strongly alkaline. When Na_2S and its hydrates is exposed to moist air, hydrogen sulfide will be emitted, which smells like rotten eggs.

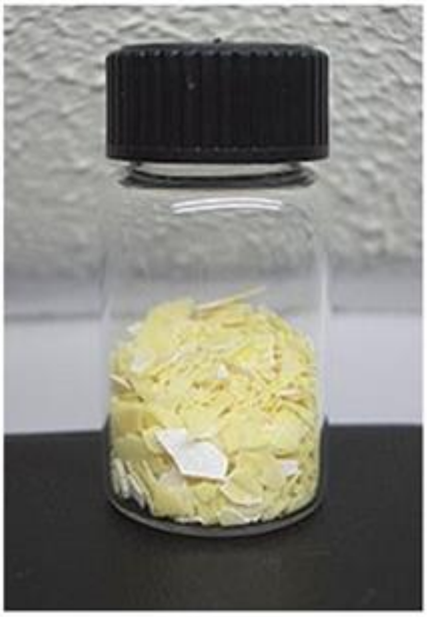


Figure 3. Photo of $Na_2S \cdot 3H_2O$ solid, used in this work to prepare Na_2S solution

Structure

Na_2S adopts the antifluorite structure, which means that the Na^+ centers occupy sites of the fluoride in the CaF_2 framework, and the larger S^{2-} occupy the sites for Ca^{2+}. In solution, the salt, by definition, dissociates. The dianion S^{2-} does not, however, exist in appreciable amounts in water. Sulfide is too strong a base to coexist with water [34].

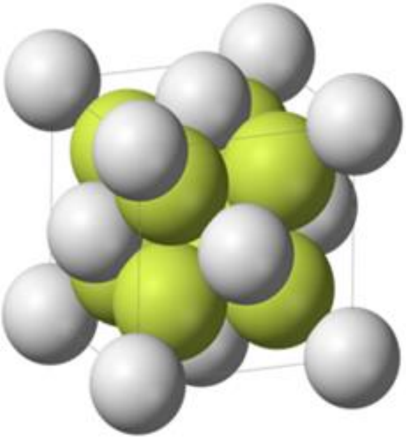


Figure 4. Structure of sodium sulfide, white ball S^{2-}, yellow ball Na^+

Production

Industrially Na_2S is produced by reduction of Na_2SO_4 with carbon, in the form of coal [35]:

$$Na_2SO_4 + 4\ C \rightarrow Na_2S + 4\ CO \qquad \text{(eq.5)}$$

In the laboratory, the anhydrous salt can be prepared by reduction of sulfur with sodium in anhydrous ammonia. Alternatively, sulfur can be reduced by sodium in dry THF with a catalytic amount of naphthalene [36]:

$$2\ Na + S \rightarrow Na_2S \qquad \text{(eq.6)}$$

Reactions

The dissolution process can be described as follows:

$$Na_2S + H_2O \rightarrow 2Na^+ + HS^- + OH^- \qquad \text{(eq.7)}$$

Sodium sulfide can oxidize when heated together with sodium carbonate and sulfur dioxide:

$$2\ Na_2S + 3\ O_2 + 2\ CO_2 \rightarrow 2\ Na_2CO_3 + 2\ SO_2 \qquad \text{(eq.8)}$$

Upon treatment with sulfur, polysulfides are formed:

$$2Na_2S + S_8 \rightarrow 2\ Na_2S_5 \qquad \text{(eq.9)}$$

Uses

- In pulp and paper industry in the craft process
- In water treatment as an oxygen scavenger agent.
- As a metals precipitant, in the photographic industry to protect developer solutions from oxidation
- In textile industry as a bleaching, desulfurising and dechlorinating agent
- In leather trade for the sulfitisation of tanning extracts.
- In chemical manufacturing as a sulfonation and sulfomethylation agent
- In the production of rubber chemicals, sulfur dyes and other chemical compounds
- In ore flotation, oil recovery, food preservative, making dyes, and detergent.

Safety

Sodium sulfide is an active ingredient in some over-the-counter ingrown toenail relief products. Like sodium hydroxide, sodium sulfide is strongly alkaline and can cause skin burns. Acids react with it to rapidly produce hydrogen sulfide, which is a toxic and foul-smelling gas.

CAS Number: 1313-82-2

R-phrases: R31, R34, R50

S-phrases: (S1/2), S26, S45, S61

3.1.2 Ammonium sulfide

Ammonium sulfide, also known as diammonium sulfide, is an unstable salt with the formula $(NH_4)_2S$. Aqueous solutions purporting to contain this salt are commercially available. With a pK_a exceeding 15 [37], the hydrosulfide ion cannot be deprotonated to an appreciable amount by ammonia. Thus, such solutions mainly consist of a mixture of ammonia and $(NH_4)SH$.

Figure 5. Photo of ammonium sulfide solution

Preparation

Ammonium sulfide is prepared from reacting hydrogen sulfide with excess amounts of ammonia:

$$H_2S + 2\,NH_3 \rightarrow (NH_4)_2S \qquad \text{(eq.10)}$$

Uses

Ammonium sulfide is used in photographic developing, to apply patina to bronze, and in textile manufacturing. Also, due to its offensive smell, it is the active ingredient in a variety of foul pranks including the common stink bomb.

Safety

Solutions of "ammonium sulfide" are hazardous as labile sources of toxic hydrogen sulfide [38].

CAS number: 12135-76-1

R-phrases: R31, R34, R50

S-phrases: (S1/2), S26, S45, S61

3.1.3 *Ammonium polysulfide*

Ammonium polysulfide is a clear, yellow to red liquid with a rotten egg or ammonia-like odor. It is used as an analytical reagent and an insecticide. It is corrosive to eyes and skin. Ingestion severely burns and corrodes all parts of the gastrointestinal tract. Inhalation of the fumes is to be avoided. When heated or diluted, solutions may evolve hydrogen sulfide and ammonia vapors. It dissolves in water with some precipitation of elemental sulfur.

Figure 6. Photo of ammonium polysulfide solution

Reactions

No rapid reaction with air and no rapid reaction with water are reported for ammonium polysulfide. It is a strong reducing agent and reacts strongly alkaline in aqueous solution. It reacts with acids to generate toxic gaseous hydrogen sulfide and reacts with bases to release gaseous ammonia. Ammonium polysulfide may also react vigorously with oxidizing agents, including inorganic oxoacids, organic peroxides and epoxides.

Uses

It can be applied directly to soil as a fertilizer.

Safety

Ammonium Polysulfide is highly flammable. When contact with acids liberates toxic gas and causes burns.

CAS number: 12259-92-6

R-phrases: R31, R34, R50

S-phrases: (S1/2), S26, S45, S61

3.2 Substrates

3.2.1 Indium Arsenide (InAs)

Description

Indium arsenide is a semiconductor material made of arsenic and indium. The semiconductor has a melting point of 942 °C and appears in the form of grey crystals with a cubic structure. It is very similar to gallium arsenide and is a material exhibiting a direct band gap. Indium arsenide is popular for its narrow energy band gap and high electron mobility.

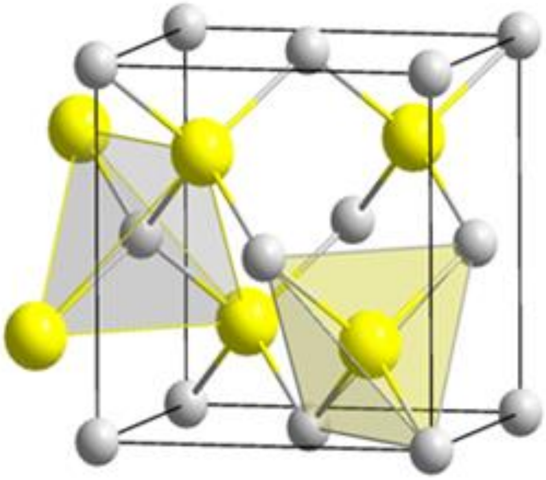


Figure 7. Structure of indium arsenide, white ball In^{3+}, yellow ball As^{3-}

Applications

The applications of indium arsenide are listed below:

- Indium arsenide is used to construct infrared detectors for a wavelength range of 1–3.8 µm. The detectors are normally photovoltaic photodiodes.
- Detectors that are cryogenically cooled have low noise but InAs detectors can be used in high-power applications at room temperature also.
- Diode lasers are also made using indium arsenide.
- Indium arsenide and gallium arsenide are similar and it is a direct band gap material.
- It is used as a terahertz radiation source.
- It is possible to form quantum dots in a monolayer of indium arsenide on gallium arsenide or indium phosphide
- It is also possible to form quantum dots in indium gallium arsenide in the form of indium arsenide dots arranged in the gallium arsenide matrix.

Chemical Properties

The chemical properties of indium arsenide are provided in the table below:

Chemical Properties	
Chemical Formula	InAs
Molecular Weight	189.74
CAS No.	1303-11-3
IUPAC Name	Indium (III) Arsenide
Group	NA
Band Gap	0.36 eV
Band Gap Type	Direct
Crystal Structure	Zinc Blende
Symmetry Group	T_d^2-F43m
Lattice Constant	6.0583 Angstroms

Table 3. Chemical properties of indium arsenide

Electrical Properties

The electrical properties of indium arsenide are provided in the table below:

Electrical Properties	
Intrinsic Carrier Concentration	$1 \times 10^{15} cm^{-3}$
Electron Mobility	$\leq 4 \times 10^{4} cm^{2}\ V^{-1}\ s^{-1}$
Hole Mobility	$\leq 5 \times 10^{2}\ cm^{2}\ V^{-1}\ s^{-1}$
Electron Diffusion Coefficient	$\leq 10^{3}\ cm^{2}\ s^{-1}$
Hole Diffusion Coefficient	$\leq 13\ cm^{2}\ s^{-1}$

Table 4. Electrical properties of indium arsenide

Thermal, Mechanical and Optical Properties

The thermal, mechanical and optical properties of indium arsenide are provided in the tables below:

Mechanical Properties	
Melting Point	942 °C
Density	5.67 g cm^{-3}
Thermal Properties	
Thermal Conductivity	0.27 W cm^{-1} °C^{-1}
Thermal Diffusivity	0.19 cm^{2} s^{-1}
Thermal Expansion Coefficient	4.52x10^{-6} °C^{-1}
Optical Properties	
Infrared Refractive Index (@300 K)	3.51
Radiative Recombination Coefficient (@ 300 K)	1.1x10^{-10} cm^{3} s^{-1}

Table 5. Mechanical, thermal and optical properties of indium arsenide

Safety Information

Safety Information	
GHS Hazard Statements	NA
Hazard Codes	T - Toxic N – Dangerous to the environment
Risk Codes organisms	R23 - Toxic by inhalation R25: Toxic if swallowed R50: Very toxic to aquatic

Table 6. Safety information of indium arsenide

HEALTH HAZARD INFORMATION

Acute Effects:

- Inhalation: May cause irritation and damage to the respiratory system.
- Ingestion: May cause systemic gastrointestinal and skin effects and acute arsenic poisoning.
- Skin: May cause skin irritation and skin abnormalities.
- Eye: May cause irritation

Chronic Effects:

- Inhalation: May cause chronic pneumonitis, arsenic poisoning, ulceration of the nasal septum, liver damage and cancer/disease of the blood, kidneys and nervous system.
- Ingestion: May cause chronic arsenic poisoning, gastrointestinal disturbances, liver damage and cancer/disease of the blood, kidneys and nervous system.
- Skin: May cause irritation, occasional ulceration, spotty pigmentation, dermatitis, skin cancer and keratosis (especially on soles and palms).
- Eye: No chronic health effects recorded.
- Routes of Entry: Ingestion, inhalation.
- Target Organs: May affect the liver, kidneys, skin, lungs and lymphatic system.
- Medical Conditions Generally Aggravated by Exposure: Pre-existing respiratory disorders.

3.2.2 Gallium Arsenide (GaAs)

Description

Gallium arsenide is a type III/V semiconductor, with high electron mobility and a high saturation electron velocity compared to silicon, enabling transistors made of gallium arsenide to function at frequencies over 250 GHz.

Gallium arsenide devices are not sensitive to heat because of their wide band gap. Also, these devices typically have less noise than silicon devices, especially at high operating frequencies.

GaAs has held great interest for use in semiconductor/liquid junction photo electrochemical solar cell applications due to its high absorption near a maximum in the solar energy spectrum.

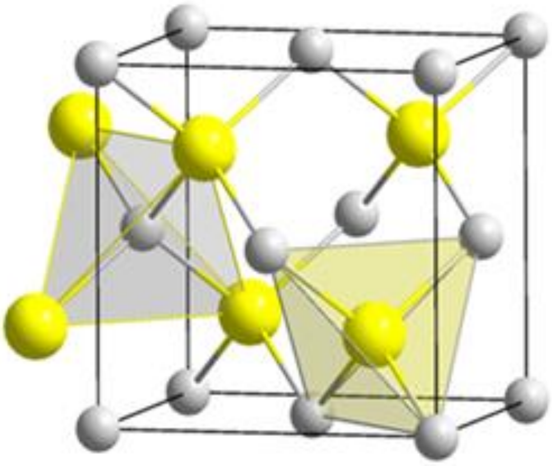


Figure 8. Structure of gallium arsenide, white ball Ga^{3+}, yellow ball As^{3-}

Applications

The applications of gallium arsenide are listed below:

- Gallium arsenide can be used to manufacture devices such as monolithic microwave integrated circuits, microwave frequency integrated circuits, infrared light-emitting diodes, solar cells, laser diodes and optical windows.
- GaAs has a direct band gap unlike many other semiconductors implying it can emit light with high efficiency. Being a direct band gap material, it is resistant to radiation damage enabling its use in optical windows and space electronics in high power applications.
- Solar cells based on GaAs power the Opportunity and Spirit rovers that are exploring the surface of Mars. A number of solar cars make use of GaAs in solar arrays.

Chemical Properties

The chemical properties of gallium arsenide are provided in the table below:

Chemical Properties	
Chemical Formula	GaAs
Molecular Weight	144.645
CAS No.	1303-00-0
IUPAC Name	Gallium Arsenide
Group	III-V
Band Gap	1.424 eV
Band Gap Type	Direct
Crystal Structure	Zinc Blende
Symmetry Group	T_d^2-F43m
Lattice Constant	5.4505 Å

Table 7. Chemical properties of gallium arsenide

Electrical Properties

The electrical properties of gallium arsenide are provided in the table below:

Electrical Properties	
Intrinsic Carrier Concentration	1.79×10^6 cm^{-3}
Electron Mobility	≤ 8500 cm^2 V^{-1} s^{-1}
Hole Mobility	≤ 400 cm^2 V^{-1} s^{-1}
Electron Diffusion Coefficient	≤ 200 cm^2 s^{-1}
Hole Diffusion Coefficient	≤ 10 cm^2 s^{-1}

Table 8. Electrical properties of gallium arsenide

Thermal, Mechanical and Optical Properties

The thermal, mechanical and optical properties of Gallium Arsenide are provided in the tables below:

Mechanical Properties	
Melting Point	1238 °C
Density	5.3176 g cm^{-3}
Young's Modulus	82.68 GPa
Bulk Modulus	75.5 GPa

Thermal Properties	
Thermal Conductivity	0.55 W cm^{-1} $°C^{-1}$
Thermal Diffusivity	0.31 cm^2 s^{-1}
Thermal Expansion Coefficient	5.73×10^{-6} $°C^{-1}$

Optical Properties	
Refractive Index (589 nm @ 293 K)	3,3
Radiative Recombination Coefficient (@ 300 K)	7×10^{-10} cm^3 s^{-1}

Table 9. Mechanical, thermal and optical properties of gallium arsenide

Safety Information

Safety Information	
GHS Hazard Statements	NA
Hazard Codes	T-Toxic，N - dangerous for the environment
Risk Codes	R23 - Toxic by inhalation R25: Toxic if swallowed R50: Very toxic to aquatic organisms R53: May cause long-term adverse effects in the aquatic environment
Safety Precautions	S 20/21-28-45-60-61

Table 10. Safety information of gallium arsenide

4. Experimental setup

4.1 Photoluminescence spectroscopy

Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. In the PL experiment, a semiconductor was excited with a light-source (Diode laser in this work) that provides photons with energy larger than the band gap energy.

Once the photons were absorbed, electrons and holes were respectively formed with finite momenta in the conduction and valence bands. The excitations then undergo energy and momentum relaxation towards the band gap minimum. Typical mechanisms were Coulomb scattering and the interaction with phonons. Finally, when defect and impurity are free in the band gap, the electrons recombined with holes under emission of photons.

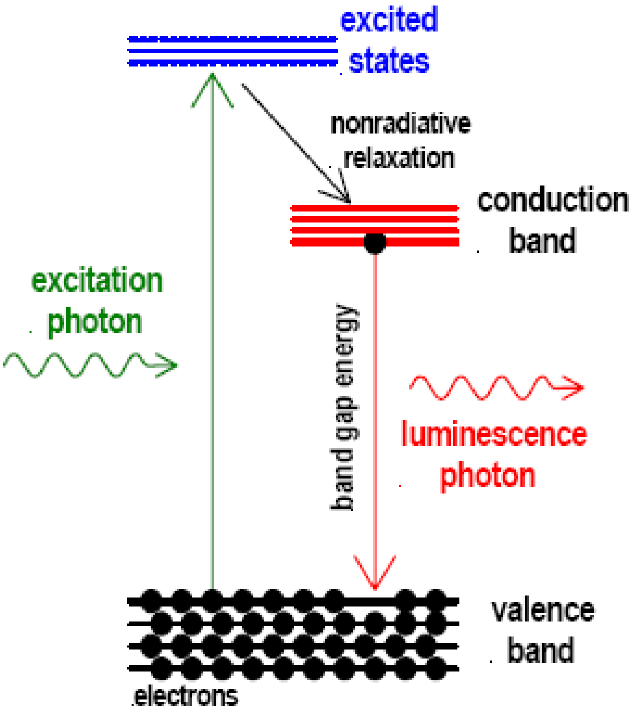


Figure 9. Photoluminescence principle

However, if many non-radiative recombination centers are present due to defects related to energy states in the bulk and surface states at the interface located within the band gap, the recombination occuring at these sites will not generate photons but only phonons. The PL intensity is reduced. Therefore, the intensity of the PL signal provides information on the nature of surfaces and interfaces.

PL analysis is mostly nondestructive. The advantage of PL measurement is, that the technique requires very little sample manipulation or environmental control. Because the sample is excited optically, electrical contacts and junctions are unnecessary and high-resistivity materials pose no practical difficulty. In addition, time-resolved PL can be very fast, making it useful for characterizing the most rapid processes in a material.

On the GaAs surface it’s easy to form surface states leading to non-radiative recombination centers. Comparing the PL intensity before and after passivation under the same excitation laser power, we can clearly see if these surface states are removed.

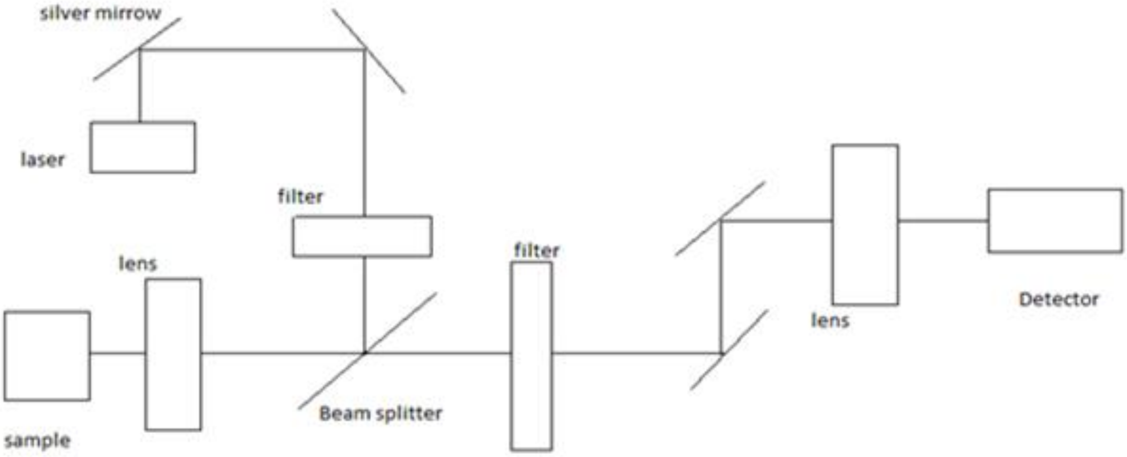


Figure 10. Schematics of the photoluminescence spectroscopy setup

The PL setup we used is shown in Figure 10. The laser is a diode laser from PicoQuant which has a wavelength of 405nm. This wavelength can be easily absorbed in the surface of GaAs sample, and is therefore very sensitive to the surface condition. The PL signal from the GaAs was directed through a beam splitter and a filter into a CCD camera, which records the PL spectra. The spectral range that we studied is from 736 to 1014nm. Because of the setup limitation, all the GaAs samples have to be tested in contact with air under room temperature.

In this work, only GaAs samples were measured by PL spectroscopy. The band gap of InAs is about 0.36eV, thus the wavelength is about 3444nm, which exceeds the range of CCD detector.

4.2 x-ray photoelectron spectroscopy

Theory

X-ray Photoelectron Spectroscopy (XPS), also known as ESCA, is a surface analysis technique that uses an x-ray beam to eject electrons from a surface.

The kinetic energies of the ejected electrons (photoelectrons) are then analyzed to produce a spectrum, in which photoelectron peaks coming from different chemical elements can be identified by their characteristic energies. The typical sample areas that can be analyzed are between 1 mm^2 and 1 cm^2, which make XPS a useful technique for studying a wide variety of samples.

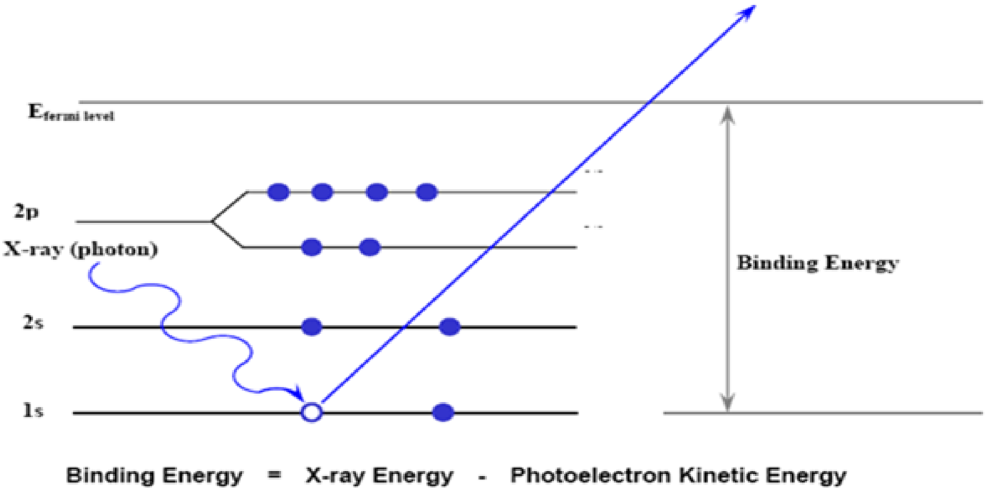


Figure 11. Principle of photoelectron generation

Measurement

XPS is used to determine:

- Elemental composition of the surface (top 0–10 nm usually)
- Empirical formula of pure materials
- Elements that contaminate a surface
- Chemical or electronic state of each element in the surface
- Uniformity of elemental composition across the top surface (or line profiling or mapping)
- Uniformity of elemental composition as a function of ion beam etching (or depth profiling)

Because the energy of an X-ray with a particular wavelength is known (for aluminum Kα X-rays, E_{photon} = 1486.7 eV), and because the emitted electrons' kinetic energies are measured, the electron binding energy of each of the emitted electrons can be determined by using an equation that is based on the work of Ernest Rutherford (1914):

$$E_{binding} = E_{photon}-(E_{kinetic} + \varphi) \qquad \text{(eq.11)}$$

where $E_{binding}$ is the binding energy (BE) of the electron, E_{photon} is the energy of the X-ray photons being used, $E_{kinetic}$ is the kinetic energy of the electron as measured by the instrument and φ is the work function of the spectrometer (not the material). This equation is essentially a conservation of energy equation. The work function term φ is an adjustable instrumental correction factor that accounts for the few eV of kinetic energy given up by the photoelectron as it becomes absorbed by the instrument's detector. It is a constant that rarely needs to be adjusted in practice.

Surface Sensitivity

X-rays penetrate deeply into the sample surface, exciting photoelectrons. However, photoelectrons can travel only a short distance before their energy is modified due to interaction with neighboring atoms. Only photoelectrons that escape at their original energy contribute to a peak in a spectrum. This phenomenon makes XPS a very surface sensitive technique, with an average depth of analysis of 50 Angstroms.

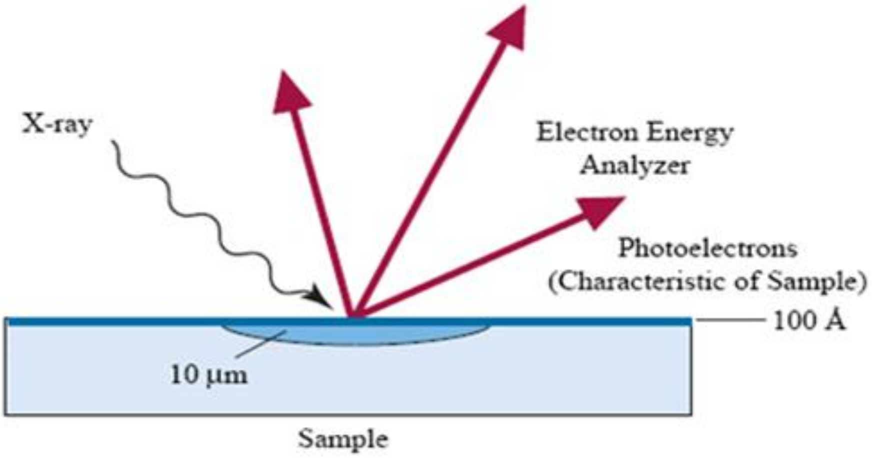


Figure 12. Phenomena of electron excitation

Chemical states from XPS analysis (the chemical shift)

The ability to produce chemical state information (as distinguished from merely elemental information) from the topmost few nm of any surface makes XPS a unique and invaluable tool for understanding the chemistry of any surface, either as received, or after physical or chemical treatment(s). In this context, "chemical state" refers to the local bonding environment of a species in question. The local bonding environment of a species in question is affected by its formal oxidation state, the identity of its nearest-neighbor atom, it's bonding hybridization to that nearest-neighbor atom, and in some cases even the bonding hybridization between the atom in question and the next-nearest-neighbor atom.

Thus, while the nominal binding energy of the C 1s electron is 284.6 eV (some also use 285.0 eV as the nominal value for the binding energy of carbon), subtle but reproducible shifts in the actual binding energy, the so-called chemical shift, provide the chemical state information referred to here.

Figure 13 presents an XPS survey spectrum of an oxidized InAs surface. The major XPS peaks are marked for In and As of the InAs substrate, as well as for C and O present on the surface.

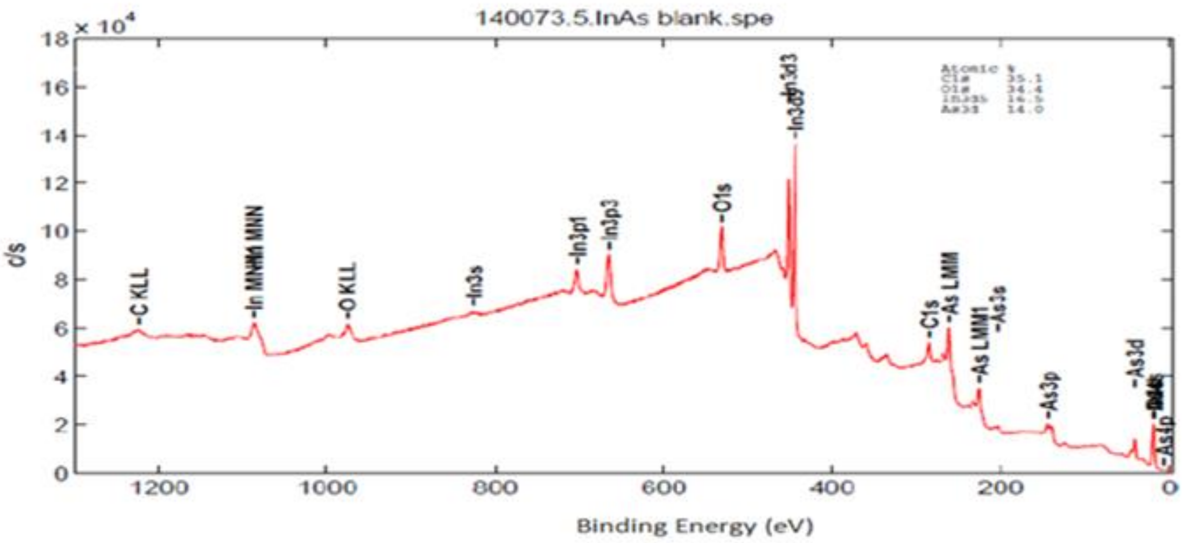


Figure 13. XPS spectrum for unpassivated InAs (110)

Quantitative Interpretation of XPS Data

In the most general case, the "atomic percent" method is used to interpret XPS data, whereby the signal from each element is normalized against the total amount of all the detected elements, which is taken as 100%. The simplicity of the "atomic percent" interpretation can be considered both as a curse and as a blessing, depending on the system being analyzed.

The main benefit of this method is that it always works and is never wrong, to the extent that the areas of all the elemental peaks in the spectrum have been determined correctly. However, taken on its own, e.g., without reference data from standard samples, the "atomic percent" composition is not particularly informative because non-uniform distribution of the different elements can strongly affect the corresponding "atomic percent" values (the apparent composition will be rich in elements that are closer to the surface).

Fortunately, more advanced XPS interpretation is possible for certain broad classes of samples, e.g., thin layers of organic molecules, polymers, or biomolecules supported on a substrate of simple and uniform composition, or thin oxide layers on metals and semiconductors. For common substrate materials (silicon, gold, aluminum, copper, silver) the corresponding material parameters (density, electron attenuation length) are well-known, allowing the interpretation of XPS data not only in terms of relative elemental concentrations, but also in terms of absolute numbers of atoms of the respective elements.

5. Experimental Preparations and Procedures

Preparation of Na_2S solution

Using $Na_2S·3H_2O$ to prepare 200mL 1mol/L Na_2S solution

$M_{Na2S·3H2O}$=132g/mol

$c_{Na2S(aq)}$=1mol/L

$V_{Na2S(aq)}$=200mL

$m_{Na2S·3H2O}=M_{Na2S·3H2O}*n_{Na2S·3H2O}= M_{Na2S·3H2O}* C_{Na2S(aq)}* V_{Na2S(aq)}=26.4g$ (eq.12)

Put 26.4g $Na_2S·3H_2O$ in container, add H_2O to 200mL, shake until the solution is homogeneous.

Preparation of $(NH_4)_2S$ solution

Using 20% $(NH_4)_2S$ solution to prepare 1mol/L $(NH_4)_2S$ solution

$M_{(NH4)2S}$=68g/mol

$c_{(NH4)2S(aq)}=0.2*\rho_{(NH4)2S(aq)}/M_{(NH4)2S}=3mol/L$ (eq.13)

20%$(NH_4)_2S_{(aq)}$: H_2O =1: 2 diluted

Freshly prepared, shake until the solution is homogeneous.

Preparation of $(NH_4)_2S_x$ solution

Using 9mol/L $(NH_4)_2S_x$ solution to prepare 1mol/L $(NH_4)_2S_x$ solution

$(NH_4)_2S_{x(aq)}$: H_2O =1: 8 diluted

Freshly prepared, shake until the solution is homogeneous.

Substrates

Substrates indium arsenide and gallium arsenide were cut into 1*1 cm^2 pieces, Investigation with XPS of 110-oriented InAs surface in comparison to 110-oriented GaAs surface without any pretreatment, determination of surface impurities.

6. Experimental Procedures and Results

6.1 Surface passivation of Gallium Arsenide

Undoped (110)-oriented GaAs were treated with 1mol/L sodium sulfide, ammonium sulfide or ammonium polysulfide aqueous solution for 5min without preliminary etching. Then the samples were rinsed in deionized water. Samples without any treatment were used as reference.

Nr.	treatment
1.1	Without any treatment
1.2	Immersed in 1mol/L Na_2S solution, rinsed by DI water, dried with N_2
1.3	Immersed in 1mol/L $(NH_4)_2S$ solution, rinsed by DI water, dried with N_2
1.4	Immersed in 1mol/L $(NH_4)_2S_x$ solution, rinsed by DI water, dried with N_2

Table 11. Treatments of gallium arsenide (110) to compare the effect of different sulfide solutions removal the oxides layer on the surface

The determination of the optimum treatment becomes an important problem. When the treatment time is too short, the formation of a complete chemisorbed sulfide monolayer on the surface can't be provided. When it's too long, a thick layer consisting of elemental sulfur, which necessarily appears in sulfide solutions in contact with air, can be formed on the surface due to the physical sorption. According to the report of T.V.L'vova [39], we decided on the treatment time of 5min.

After passivation the samples are immediately studied by PL measurements. Figure 14 shows the PL intensities of the 4 samples under the same excitation laser power of 4.6mW.

The maximum PL signal was recorded similar to the characteristic value for this sample. The wavelength of the peak maximum (876nm) did not shift noticeably after any of the surface treatments. It is obvious that the intensities of the samples treated with the different chemicals are higher than the untreated one. In addition, the $(NH_4)_2S_x$ treated sample exhibits the highest intensity than Na_2S and $(NH_4)_2S$ treated GaAs, even 10 times higher than the reference sample.

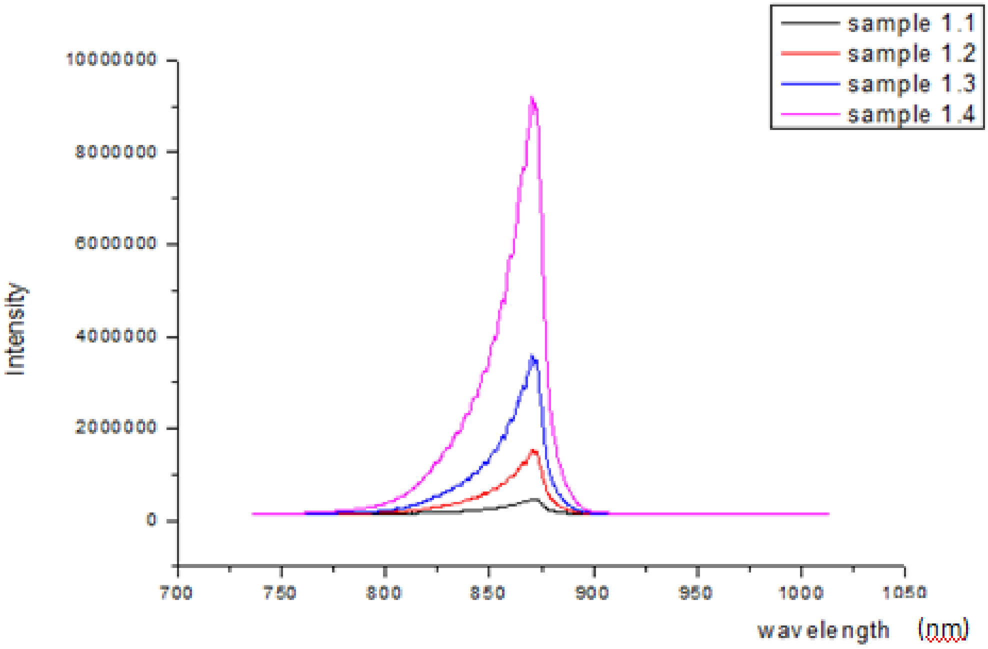


Figure 14. Photoluminescence spectra for sample 1.1 untreated GaAs (black), sample 1.2 Na_2S treated GaAs (red), sample 1.3 $(NH_4)_2S$ treated GaAs (blue) and sample 1.4 $(NH_4)_2S_x$ treated GaAs (pink)

It has been shown that a local modification on a semiconductor can be used to optimize the relevant functional properties. Focused laser beams have been used for a long time for material processing for many different purposes. Among these are laser induced crystallization, annealing, doping, alloying, oxidation and interdiffusion. Laser induced processing enables high spatial resolution and position control.

To determine the effect of laser heating, the following samples have been made

Nr.	treatment
2.1	Without any treatment
2.2	Immersed in 1mol/L Na_2S solution, rinsed by DI water, dried with N_2
2.3	Immersed in 1mol/L $(NH_4)_2S$ solution, rinsed by DI water, dried with N_2
2.4	Immersed in 1mol/L $(NH_4)_2S_x$ solution, rinsed by DI water, dried with N_2
2.5	First washed by acetone, then isopropanol, dried with N_2

Table 12. Treatments of gallium arsenide (110) for the investigation of the effect of the laser on photoluminescence

All the 5 gallium arsenide samples were heated at ambient conditions by a focused laser beam of 4.6mW for 45 seconds. During the radiation the PL was recorded every 5 seconds. The acquisition time was about 3.8s for every time. The vertical axis was the peak value at about 876nm in relation to the peak value measured at the initial acquisition time.

All five samples obviously lose intensity as the laser irradiation increases. The strongest effect is observed for the treated samples. For sample 2.1 and 2.5, there was no big difference between unwashed and organic solution washed sample. Among the three sulfur-treated samples, the $(NH_4)_2S_x$ treated sample (sample 2.4) lost less intensity than the other two samples.

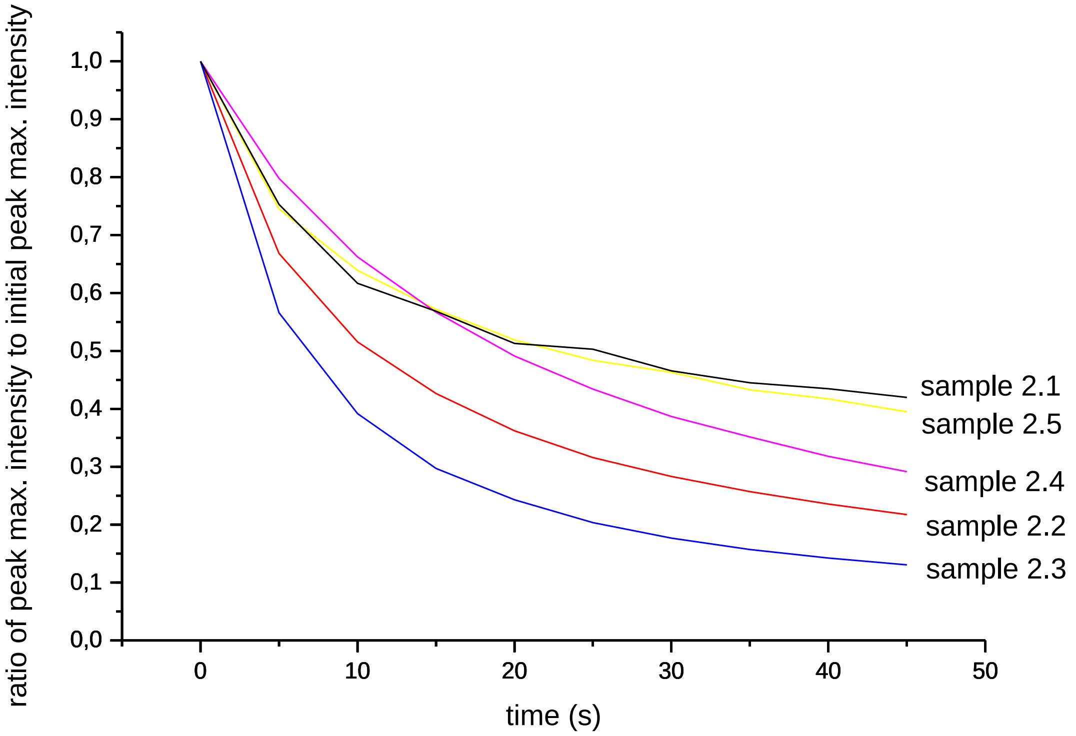


Figure 15. Development of the ratio of peak maximum intensity to initial peak maximum intensity with time for a laser power of 4.6 mW for sample 2.1 untreated GaAs (black), sample 2.2 Na_2S treated GaAs (red), sample 2.3 $(NH_4)_2S$ treated GaAs (blue), sample 2.4 $(NH_4)_2S_x$ treated GaAs (pink) and sample 2.5 organic solution washed GaAs (yellow)

Laser intensity also influences the PL quenching. For the Na_2S treated sample, the intensity of GaAs decreases faster at a laser power of 5.4mW than at 4.6mW. Influence of different laser powers for GaAs samples treated with Na_2S and a laser power of 5.4mW and 4.6mW is shown in Fig. 16.

After the experiment above, we maintained the laser irradiation, and repeated the measurements several times until the PL intensity was quite stable. The time interval was about 5min. The long term PL intensity is plotted in Fig. 17.

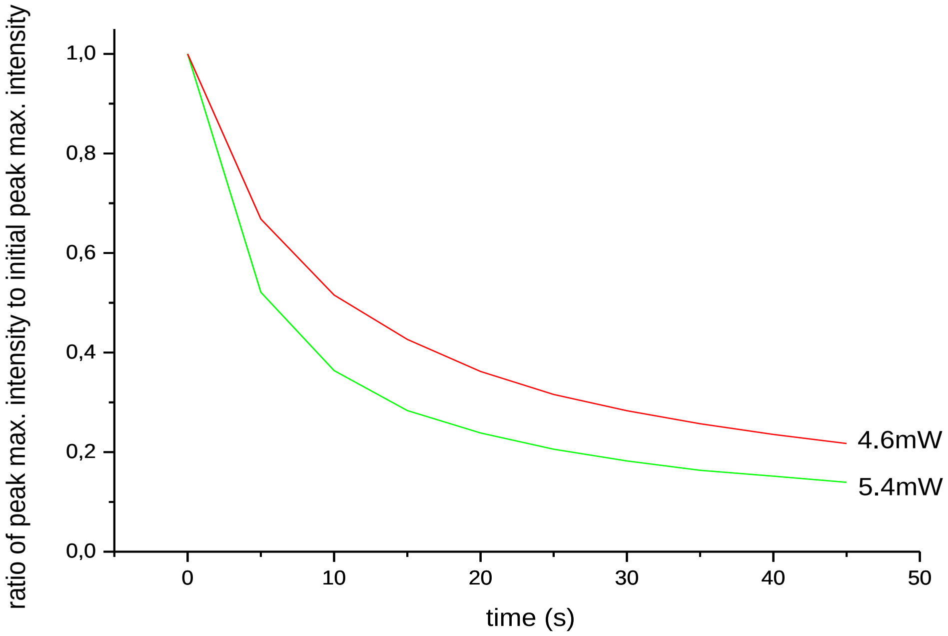


Figure 16. Influence of different laser powers for GaAs samples treated with Na_2S under a laser power of 5.4mW (green) and 4.6mW (red), respectively.

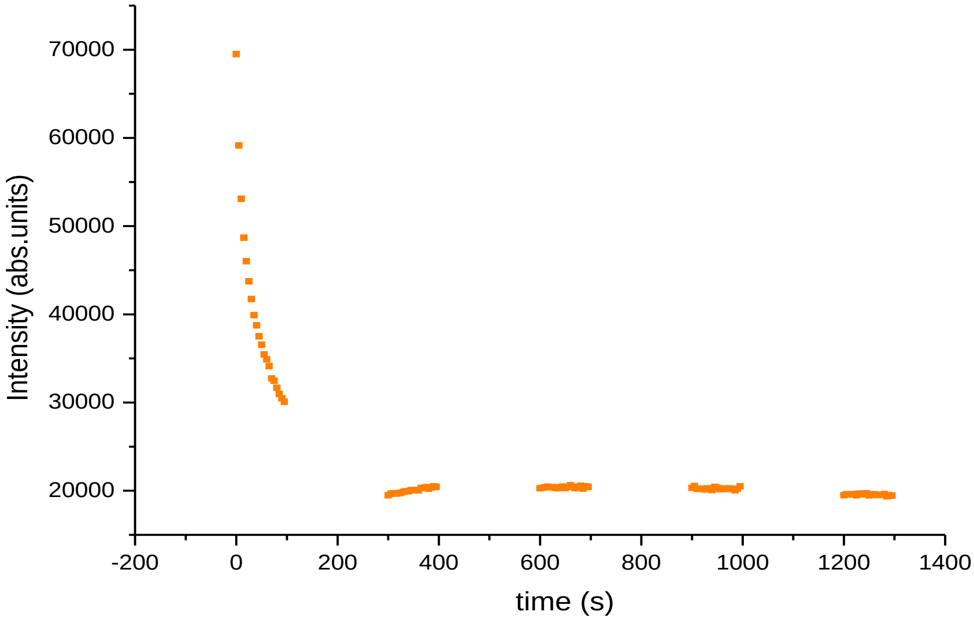


Figure 17. Intensity change by laser irradiation of Na_2S treated GaAs (110) under power of 4.6mW

After 10 minutes of continuous laser irradiation at a power of 4.6mW, the GaAs sample treated with Na_2S exhibits a constant and stable intensity. Similar results were observed for the other sulfide treated samples.

Interpretation of the results: Untreated GaAs surfaces react with oxygen form the air to form oxides according to the following equations.

$$3O_2 + 2GaAs \rightarrow As_2O_3 + Ga_2O_3 \qquad \text{(eq.14)}$$

$$As_2O_3 + 2GaAs \rightarrow Ga_2O_3 + 4As \qquad \text{(eq.15)}$$

or

$$4O_2 + 2GaAs \rightarrow As_2O_5 + Ga_2O_3 \qquad \text{(eq.16)}$$

$$3As_2O_5 + 10GaAs \rightarrow 5Ga_2O_3 + 16As \qquad \text{(eq.17)}$$

The great enhancement of the PL intensity shown in figure 14 after the treatment with sulfide passivation chemicals indicates that a chemical reaction has taken place and that the oxides on GaAs surface have been removed. It seems that the treatments are differently effective in removing the oxides and replacing them by a passivation coating. $(NH_4)_2S_x$ is more efficient than Na_2S or $(NH_4)_2S$ is presented. Mechanisms for the formation of a "passivating" coating on various III/V semiconductors treated with $Na_2S{\cdot}3H_2O$ dissolved in water have already been proposed by Bessolov and are described in the following equations. [40] [41]

$$Na_2S + H2O \rightleftarrows 2Na^+ + HS^- + OH^- \qquad \text{(eq.18)}$$

$$x\ A^{III}B^{V} + 2y\ HS^- + 2y\ H2O \rightleftarrows A_xS_y + B_xS_y + 2y\ OH^- + 2y\ H_2\,(g) \qquad \text{(eq.19)}$$

Where A and B are the group III and Ⅴ elements respectively and x and y represent the stoichiometric coefficients.

The chemistry related to the treatment with $(NH_4)_2S$ is proposed to proceed as follows:

$$(NH_4)_2S \rightarrow 2NH_4{}^+{}_{aq} + S^{2-}{}_{aq} \qquad \text{(eq.20)}$$

$$NH_4{}^+ + H_2O \rightarrow NH_3 + H_3O^+ \qquad \text{(eq.21)}$$

The results presented in this work verify that treatment with Na_2S solution results in partial removal of metal oxides. The small amount of H_3O^+ present through the hydrolysis reaction removes more oxides from the GaAs surface.

The effect of local laser induced modification of GaAs was observed. The modification may be caused heating of the surface and may initiate the formation of crystalline As on GaAs films known to be mediated by the formation of arsenic oxides [42]. They decompose at the oxide/GaAs interface following the thermally induced interfacial solid-solid reaction as:

$$As_2O_3(s) + 2GaAs(s) \rightarrow Ga_2O_3(s) + 4As(s) \qquad \text{(eq.22)}$$

The PL emission is completely suppressed in the annealed region. The structural changes are related for the first time to the thermal properties of GaAs.

These laser heating studies allow the local modification of the structure and of the semiconductor properties. The oxide/As shell induced by local laser heating leads to additional phonon scattering and thus to a change of the thermal properties of the semiconductors such as the thermal conductivity.

Fig. 15 demonstrates that the optical properties of the $(NH_4)_2S_x$ treated sample are least changed by the laser and is therefore most stable towards laser heating and oxidation in air. Unfortunately, the effect of different sulfide treatments on the InAs surface cannot be determined with our PL setup, since the setup does not have a suitable detector for extremely low band-gap materials. However, the results of the GaAs surface passivation PL study may be indirectly applied to the XPS study of passivated InAs samples.

6.2 Surface passivation of Indium Arsenide

Undoped (110)-oriented InAs wafer pieces were treated with 1mol/L sodium sulfide, ammonium sulfide or ammonium polysulfide aqueous solution for 5min. Then the samples were rinsed in deionized water. Samples without any treatment were used as a reference.

Nr.	treatment
3.1	Without any treatment
3.2A	Immersed in 1mol/L Na_2S solution, then rinsed by DI water, dried with N_2, 1st measurement directly after preparation, 2nd after 9h in UHV
3.2B	Immersed in 1mol/L Na_2S solution, then rinsed by DI water, dried with N_2, exposed to air for 24h before measurement
3.3A	Immersed in 1mol/L $(NH_4)_2S$ solution, then rinsed by DI water, dried with N_2, 1st measurement directly after preparation, 2nd after 9h in UHV

3.3B	Immersed in 1mol/L $(NH_4)_2S$ solution, then rinsed by DI water, dried with N_2, exposed to air for 24h before measurement
3.4A	Immersed in 1mol/L $(NH_4)_2S_x$ solution, then rinsed by DI water, dried with N_2, 1st measurement directly after preparation, 2nd after 9h in UHV
3.4B	Immersed in 1mol/L $(NH_4)_2S_x$ solution, then rinsed by DI water, dried with N_2, exposed to air for 24h before measurement

Table 13. Treatments of indium arsenide

XPS scans were acquired for As 3d, O 1s, C 1s, In 3d and S 2p. XPS analysis was carried out at room temperature in a UHV chamber with a base pressure below $5x10^{-9}$ mbar.

Peak name	concentration / %	measured E_B / eV	reference E_B / eV	possible compound
As 3d Doublet 1	17.9	40.9	40.7	InAs
As 3d Doublet 2	2.1	44.0	44.9	As_2O_3
As 3d Doublet 3	5.5	45.4	46.0	As_2O_5
O 1s Peak 1	32.0	531.3	530.2	In_2O_3
			531.9	As_2O_3
O 1s Peak 2	12.4	532.4	532.4	As_2O_5
In $3d_{5/2}$ Peak 1	14.6	444.4	444.5	InAs
In $3d_{5/2}$ Peak 2	15.6	445.3	445.3	InO_x

Table 14. X-ray photoelectron spectra measured peaks of untreated indium arsenide (sample 3.1)

According to the reference book of standard spectra for identification and interpretation of XPS data, we find that except doe in In - As bonds, arsenic is also present as As^{3+} and As^{5+} in arsenic oxides. Indium oxides are also detectable. InAs may react with oxygen from the ambient according to the following equations:

$3O_2 + 2InAs \rightarrow As_2O_3 + In_2O_3$ (eq.23)

$As_2O_3 + 2InAs \rightarrow In_2O_3 + 4As$ (eq.24)

or

$4O_2 + 2InAs \rightarrow As_2O_5 + In_2O_3$ (eq.25)

$3As_2O_5 + 10InAs \rightarrow 5In_2O_3 + 16As$ (eq.26)

As_2O_5 has double the concentration than As_2O_3, which means a higher oxidation state may be the stable status for arsenic. Thus, no sulfur is found on the untreated reference sample surface.

Peak name	concentration / %	measured E_B / eV	reference E_B / eV	possible compound
As 3d Doublet 1	36.2	40.9	40.7	InAs
O 1s Peak 1	10.2	531.8	531.0 531.5 531.9	Carbonates Hydroxides As_2O_3
S 2p Doublet 1	7.4	161.5	161.6 160-163	Sulfur Sulfides
In $3d_{5/2}$ Peak 1	46.2	444.4	444.5	InAs

Table 15. X-ray photoelectron spectra measured peaks of Na_2S treated indium arsenide (sample 3.2A), measured immediately after treatment

Peak name	concentration / %	measured E_B / eV	reference E_B / eV	possible compound
As 3d Doublet 1	38.5	40.7	40.7	InAs
S 2p Doublet 1	9.3	161.5	161.6 160-163	Sulfur Sulfides
In $3d_{5/2}$ Peak 1	52.2	444.3	444.5	InAs

Table 16. X-ray photoelectron spectra measured peaks of $(NH_4)_2S$ treated indium arsenide (sample 3.3A), measured immediately after treatment

Peak name	concentration / %	measured E_B / eV	reference E_B / eV	possible compound
As 3d Doublet 1	35.5	40.8	40.7	InAs
S 2p Doublet 1	169	161.6	161.6 160-163	Sulfur Sulfides
In $3d_{5/2}$ Peak 1	40.6	444.4	444.5	InAs
In $3d_{5/2}$ Peak 2	7.0	445.2	445 445.3	In-S In_2O_3

Table 17. X-ray photoelectron spectra measured peaks of $(NH_4)_2S_x$ treated indium arsenide (sample 3.4A), measured immediately after treatment

The XPS spectra of all three treatments were compared. The oxygen peak is only found in the Na_2S treated sample. Since no further arsenic or indium oxides are detectable, the oxygen contamination could originate from the ambient gas of the equipment. The observed 2p BE of 161eV is typical for sulfur in sulfides or for a chemisorbed S layer.

There is no evidence of As-S bonds which would show up as an As 3d Doublet on all three treated surfaces (Tab.15, 16, 17). For the Na_2S treated and $(NH_4)_2S$ treated samples surfaces there is no indication of In-S bonding which would evoke an In $3d_{5/2}$ Peak (Tab.15,16). However, an additional In $3d_{5/2}$ BE of 445,2eV is only observed for the $(NH_4)_2S_x$ treated indium arsenide surface. This peak can be assigned to an In-S bond if the the presence of indium oxides can be excluded (which is the case here).

Peak name	concentration / %	measured E_B / eV	reference E_B / eV	possible compound
As 3d Doublet 1	34.4	40.9	40.7	InAs
O 1s Peak 1	7.6	532.1	531.0 531.5	Carbonates Hydroxides
O 1s Peak 2	6.5	534.6	534.4	H_2O
S 2p Doublet 1	6.7	161.6	161.6	Sulfur
In $3d_{5/2}$ Peak 1	44.7	444.4	444.5	InAs

Table 18. X-ray Photoelectron Spectra measured peaks of Na_2S treated indium arsenide (sample 3.2A) after a residence time of 9h in UHV.

A comparison of the measurements on the Na_2S treated InAs before and after a nine hour UHV residence time shows, that not much difference is observed except for the additional peak of oxygen at 534.6V, may be attributed to the BE of H_2O and might also come from the remaining gas in the equipment. One possible reason could be the hygroscopicity of Na_2S, which may remain as an impurity on the InAs surface after rinsing with DI water.

Peak name	concentration / %	measured E_B / eV	reference E_B / eV	possible compound
As 3d Doublet 1	30.3	40.8	40.7	InAs
As 3d Doublet 2	1.7	44.1	44.9	As_2O_3
O 1s Peak 1	32.0	531.3	531.9	As_2O_3
S 2p Doublet 1	8.2	161.7	161.6	Sulfur
In $3d_{5/2}$ Peak 1	42.4	444.4	444.5	InAs

Table 19. X-ray Photoelectron Spectra measured peaks of Na_2S treated indium arsenide (sample 3.2B) after a residence time of 24h in air

Peak name	concentration / %	measured E_B / eV	reference E_B / eV	possible compound
As 3d Doublet 1	31.5	40.8	40.7	InAs
As 3d Doublet 2	2.2	43.7	44.9	As_2O_3
			43.7	AsS_x
O 1s Peak 1	16.1	531.2	531.9	As_2O_3
S 2p Doublet 1	6.8	161.5	161.6	Sulfur
In $3d_{5/2}$ Peak 1	43.3	444.3	444.5	InAs

Table 20. X-ray Photoelectron Spectra measured peaks of $(NH_4)_2S$ treated indium arsenide (sample 3.3B) after a residence time of 24h in air

Peak name	concentration / %	measured E_B / eV	reference E_B / eV	possible compound
As 3d Doublet 1	29.0	40.9	40.7	InAs
O 1s Peak 1	15.0	531.6	531.9	As_2O_3
			531.5	Hydroxides
S 2p Doublet 1	14.6	161.7	161.6	Sulfur
In $3d_{5/2}$ Peak 1	31.5	444.4	444.5	InAs
In $3d_{5/2}$ Peak 2	10.0	445.1	445	In-S
			445.3	In_2O_3

Table 21. X-ray Photoelectron Spectra measured peaks of $(NH_4)_2S_x$ treated indium arsenide (sample 3.4B) after a residence time of 24h in air

After 24h of air exposure, the oxygen peak of about 531eV appeared on all treated surfaces. Due to the additional peak of As 3d on Na_2S and $(NH_4)_2S$ treated surfaces, we can assume, that arsenic oxides formed. In contrast for the $(NH_4)_2S_x$ treated sample (compare Tab.17 and Tab.21), which are no additional As 3d peak after the 24h exposure to air. Here the O 1s peak could be attributed to oxygen from the ambient, which absorbed on the surface. The In-S bond is observed for the $(NH_4)_2S_x$ treated InAs surface even after 24h of air exposure.

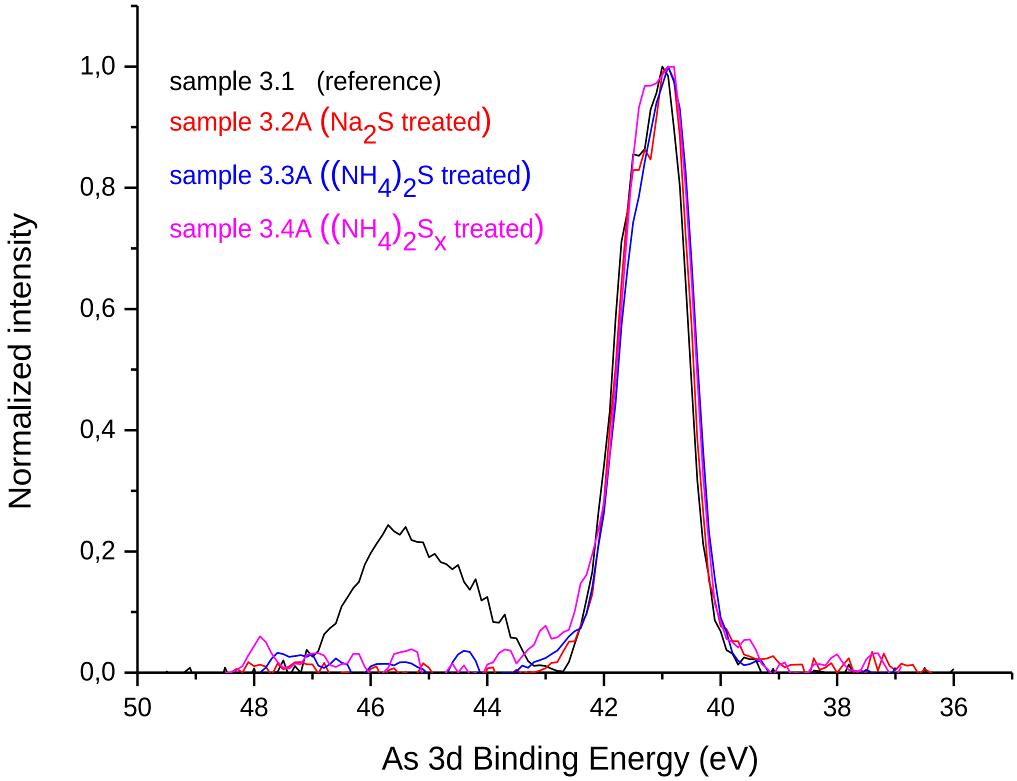


Figure 18. X-ray Photoelectron Spectra of As 3d observed for untreated (sample 3.1 black), Na_2S treated (sample 3.2A red), $(NH_4)_2S$ treated (sample 3.3A blue) and $(NH_4)_2S_x$ treated InAs surfaces (sample 3.4A pink) measured immediately after treatment

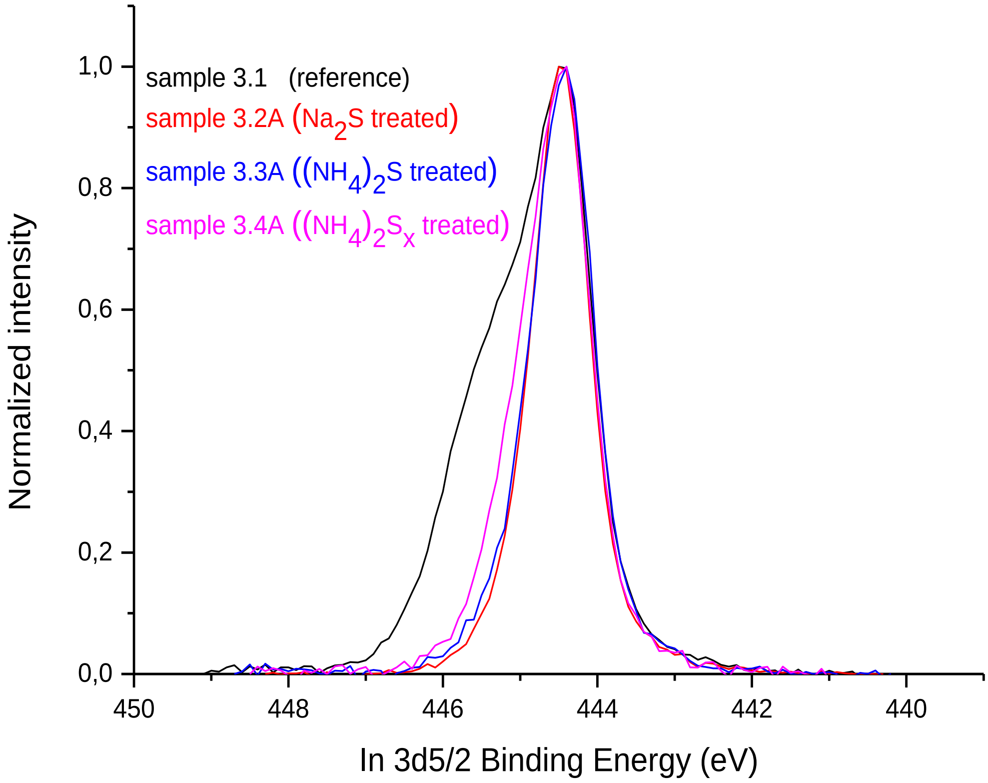


Figure 19. X-ray Photoelectron Spectra of In $3d_{5/2}$ observed for untreated (sample 3.1 black), Na_2S treated (sample 3.2A red), $(NH_4)_2S$ treated (sample 3.3A blue) and $(NH_4)_2S_x$ treated InAs surface (sample 3.4A pink) measured immediately after treatment.

For all three sulfide passivation treatments, we observe no As and In oxides peaks (As 3d and In $3d_{5/2}$) after treatment. It is evident that the treatment with Na_2S, $(NH_4)_2S$ and $(NH_4)_2S_x$ solutions completely removes arsenic oxides and indium oxides (see Fig.18 and Fig.19). As mentioned before, a higher oxidation state of +5 is more stable than a lower oxidation state of +3. The effective removal of the native As-O and In-O from InAs surface is ascribed to the chemical reactions of the sulfur based solution with the native oxides, As_2O_3, As_2O_5 and In_2O_3. In-S is observed only for the $(NH_4)_2S_x$ treated InAs surface. This may be due to the long chain of sulfur in $(NH_4)_2S_x$ solutions which creates an In-S bond more easily due to a more effective absorption than a simple sulfide anion.

A simple 'layer-cake' structure model has been proposed to describe the S-passivated InAs (001) surface, whereby a stack of alternating In and As atomic layers is passivated by a layer of S chemisorbed on the In-terminated surface. [43]

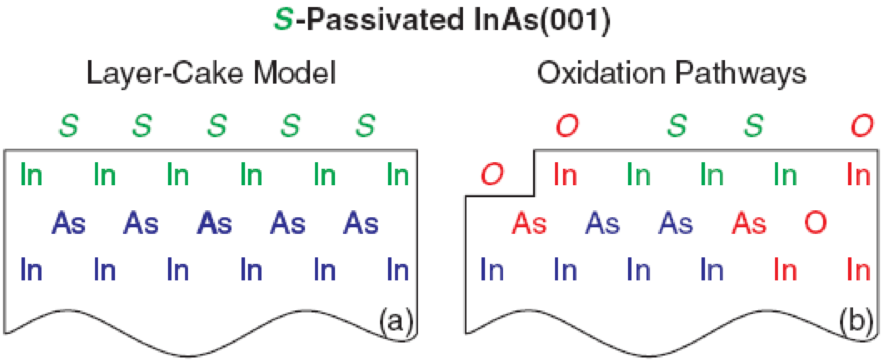


Figure 20. Schematic of a S-passivated InAs surface. (a) The idealized 'layer-cake' structure model: alternating In and As atomic layers with the top In layer terminated by the passivating S layer. (b) Potential oxidation pathways: displacement of S by O

This is an unusually simple model for a S-passivated III-V semiconductor. In contrast, on the prototypical S-passivated GaAs (001) surface, both Ga-S and As-S components are observed, along with elemental As [44]. The nearly ideal In-S termination on InAs (001) is likely a result of solubility differences between In-S and As-S in the basic passivating solutions [45].

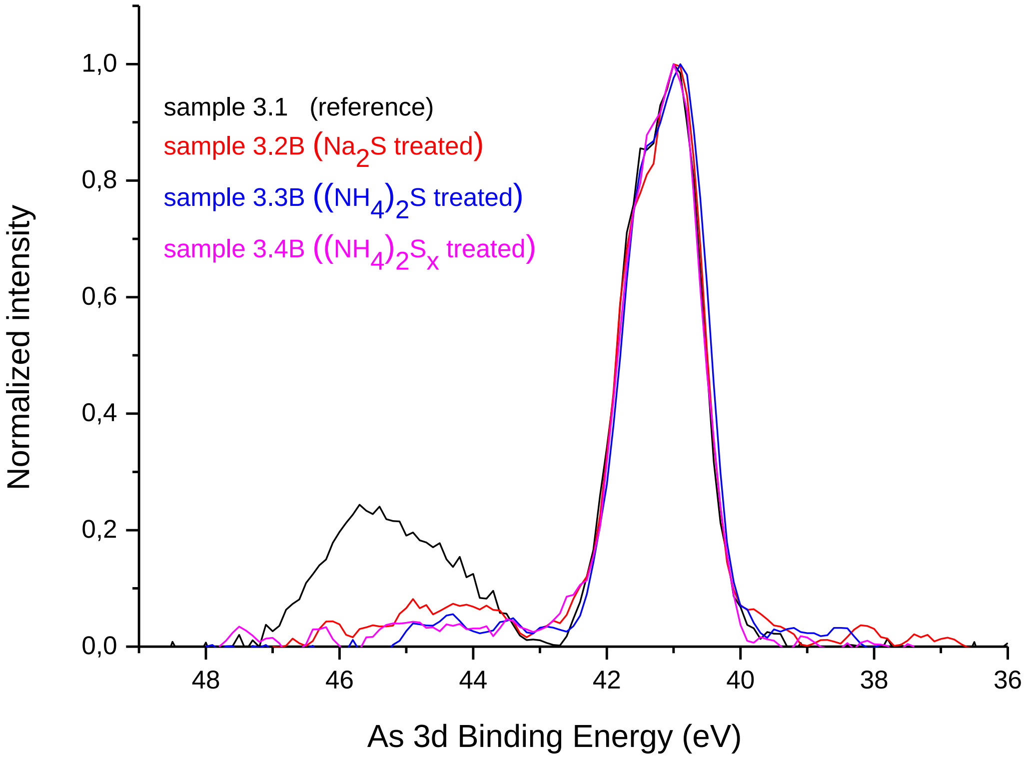


Figure 21. X-ray Photoelectron Spectra of As 3d observed for untreated (sample 3.1), Na_2S treated (sample 3.2B), $(NH_4)_2S$ treated (sample 3.3B) and $(NH_4)_2S_x$ treated InAs surface (sample 3.4B) after 24h exposure to air.

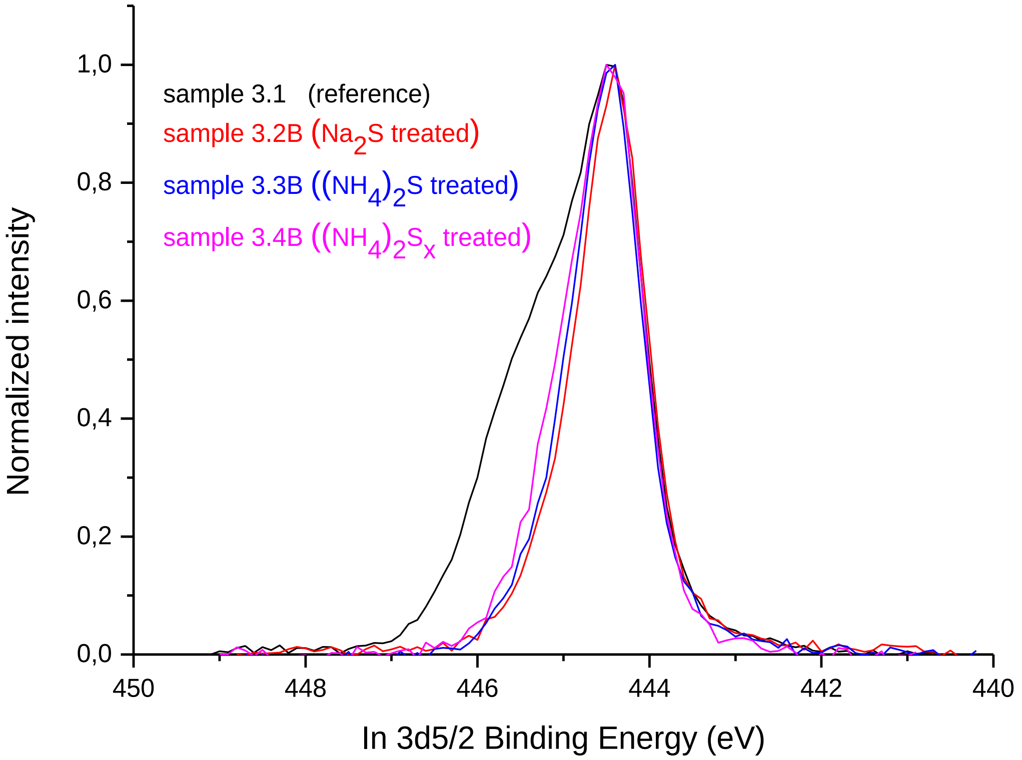


Figure 22. X-ray Photoelectron Spectra of In 3d$_{5/2}$ observed for untreated (sample 3.1), Na$_2$S treated (sample 3.2B), (NH$_4$)$_2$S treated (sample 3.3B) and (NH$_4$)$_2$S$_x$ treated InAs surfaces (sample 3.4B) after 24h exposure to air.

It is clear from Fig.21 that only in the case of Na$_2$S and (NH$_4$)$_2$S treatments, As$_2$O$_3$ forms after 24h air exposure, in contrast to the (NH$_4$)$_2$S$_x$ treatment. The arsenic oxidized more easily to the lower oxidation state of +3 than to +5. The (NH$_4$)$_2$S$_x$ treatment has longer term stability in air than the others.

There isn't much difference of In 3d$_{5/2}$ after 24h. Therefore the oxidation may begin with the As atom and later In atom.

7. Summary

In this thesis, the effect of three different passivation chemicals - Na_2S, $(NH_4)_2S$ and $(NH_4)_2S_x$ solutions – on the surface characteristics of two different substrates – GaAs and InAs was studied.

Photoluminescence spectroscopy (PL) was employed to evaluate the effect of passivation treatment on GaAs substrate surfaces (PL of the InAs samples could not be observed with our setup due to its very low band gap) and X-ray photoelectron spectroscopy (XPS) was employed for InAs substrate surfaces (here GaAs could not be studied due to the similarity of binding energies to the elements of interest).

For GaAs substrates, chemical reactions so that the oxides on the GaAs surface are more or less removed by all three sulfide passivation treatments. The PL intensity increased greatly for all three treatments compared to untreated samples. There is an indication, however, that $(NH_4)_2S_x$ is more efficient than Na_2S or $(NH_4)_2S$ in the removal of the natural oxides and replacing them by a passivation coating.

The effect of local laser induced modification of the GaAs was observed. Such modification may be caused by a heating of the surface and may initiate the formation of crystalline As on GaAs films known to be mediated by the formation of arsenic oxides. The optical properties of the $(NH_4)_2S_x$ treated sample are least changed by the laser and is therefore most stable towards laser heating and oxidation in air.

For the XPS studies on the InAs surfaces passivated by the sulfide solutions mentioned above we find, that the treatments very effectively remove native oxides (i.e a large amount of As_2O_5 and small amounts of As_2O_3 or In_2O_3).

An In-S bond is observed only for the $(NH_4)_2S_x$ treated InAs surface. There is an indication that it is more easily formed in a polysulfide solution compared to sulfide solutions due to a more effective absorption of long chain molecules. Also the $(NH_4)_2S_x$ treatment has longer term stability in air and protects the surfaces from oxidation. No oxides were detectable even after a 24h exposure in air, while the InAs surface oxidized in other sulfid solitions to form As_2O_3.

All in all $(NH_4)_2S_x$ solutions are suitable to provide an effective passivation to InAs and GaAs surfaces. The solution removes oxides, stabilizes the substrates` optical properties, protects their surfaces from oxidation and helps fill surface states.

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