URC97136

Characterizing Surfaces of the Wide Bandgap Semiconductor Ilmenite with Scanning Probe Microcopies

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Abstract:

Ilmenite ($FeTiO_3$) is a wide bandgap semiconductor with an energy gap of about 2.5eV. Initial radiation studies indicate that ilmenite has properties suited for radiation tolerant applications, as well as a variety of other electronic applications. Two scanning probe microscopy methods have been used to characterize the surface of samples taken from Czochralski grown single crystals. The two methods, atomic force microscopy (AFM) and scanning tunneling microscopy (STM), are based on different physical principles and therefore provide different information about the samples. AFM provides a direct, three-dimensional image of the surface of the samples, while STM give a convolution of topographic and electronic properties of the surface. We will discuss the differences between the methods and present preliminary data of each method for ilmenite samples.

Introduction:

The progress of technology creates new demands for discovering and developing new electronic materials with increasingly improved properties. Of particular interest to NASA are those materials that allow both space and commercial applications. Wide bandgap semiconductors like ilmenite have properties that make them attractive for a variety of applications in both the terrestrial and space realms. Wide bandgap semiconductors have potential use in high power, high frequency, high temperature microelectronic and optoelectronic (including photovoltaic) devices which are also resistant to radiation damage.

To exploit an electronic material for these types of applications, the properties of the surface are essential for developing optimum processing procedures for device fabrication. Two new surface analysis tools proved useful in microelectronic fabrication: Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM). These microcopies have resolution at the atomic level, yet can be used to examine device geometries in ultra-large scale integration ULSI circuits[1].

This paper will discuss ilmenite and some of its potential applications. We will then briefly introduce the AFM and STM techniques, discussing the information these methods provide and their limitations. We then present and discuss preliminary AFM and STM data characterizing ilmenite surfaces.

Ilmenite:

Large, high quality Czochralski grown single crystals have been produced to evaluate the materials performance for a number of applications[2]. In particular, the photovoltaic, optoelectronic, and the high radiation resistant characteristics of ilmenite seem to offer superior performance compared to traditional semiconductors. For instance, silicon solar cell has been the mainstay power conversion source for the U.S. space program. However, the conversion efficiency of Si seems to be bound at an upper limit of ~30%, and this efficiency degrades with time[3]. In addition, a wide bandgap semiconductor such as ilmenite can take advantage of the lower wavelength end of the solar spectrum. Other potential space application benefits of ilmenite include:

- Weight Savings: Extensive cooling equipment is required for Si based electronic on spacecraft. Much of this equipment could be eliminated using a large band gap material such as ilmenite.
- Radiation Resistance: Electronics in space operate without the benefit of the atmosphere to shield them from the relatively high ambient radiation environment. Ilmenite has appears to have radiation resistant properties[4].

Potential commercial applications of ilmenite include:

- Optoelectronic Devices: Ilmenite appears to have a direct bandgap making it a candidate for blue-green lasers diodes.
- Thermoelectric Coolers: Initial measurements of Seebeck coefficients appear to make ilmenite attractive in refrigeration and cooling systems.
- Heterostructures of Ilmenite: The interesting annealing properties of ilmenite (which effect the oxidation state of the iron) may provide the means for creating “seamless” interfaces between areas of n- and p-type material, perhaps leading to tunable bandgaps.

Ilmenite can be grown both an p-type and an n-type semiconductor making bipolar junction devices consisting of alternate n- and p-type materials possible. Some of ilmenite's basic properties are summed up in Table I.

Physical Property	Ilmenite $FeTiO_3$
Bandgap	2.58 eV direct(?)
Crystal Structure	Corundum (Al_2O_3)
Unit Cell	Hexagonal
a	5.09 A
c	14.09 A
c/a	2.77
Resistivity	1.45 Ωm
Hall coefficient	$0.26 * 10^{-5} m^3/C$
Carrier Concentration	$2.6 * 10^{+24} m^{-3}$
Density	$4.83 gm/cm^3$
p-type semiconductor	pure ilmenite
n-type semiconductor	in solution with $a\text{-}Fe_2O_3$
Melting point	1410°C

TABLE I: Properties of Ilmenite

Scanning Probe Microscopy:

Scanning probe microscopy techniques have gone from Nobel Prize winning discovery to production line characterization [5] in a little over a decade. Starting with the scanning tunneling microscope (STM) in 1982 [6], many different SPM techniques have been described in the literature [7]. These microscopes allow surface characterization of both conductors and insulators with sub-nanometer resolution.

Atomic Force Microscopy: Figure 1 shows a schematic of an AFM configuration. The AFM monitors the minute forces between a cantilevered probe tip and a sample surface. When the tip is scanned parallel to the sample, surface topography will tend to deflect the cantilever. The deflection is detected by reflected laser light via a photodetector. A feedback circuit monitoring this deflection controls a piezoelectric element (not shown in Figure 1) which moves the sample to counter the cantilever deflection. In effect, this keeps the force between tip and sample constant. The signal to the piezo is monitored and a topographic image is constructed from this signal as the probe is raster scanned (also by piezo elements not shown) across the sample. The typical value of force involved with AFM is 10^{-9}N, and examples of true atomic resolution have been obtained[8].

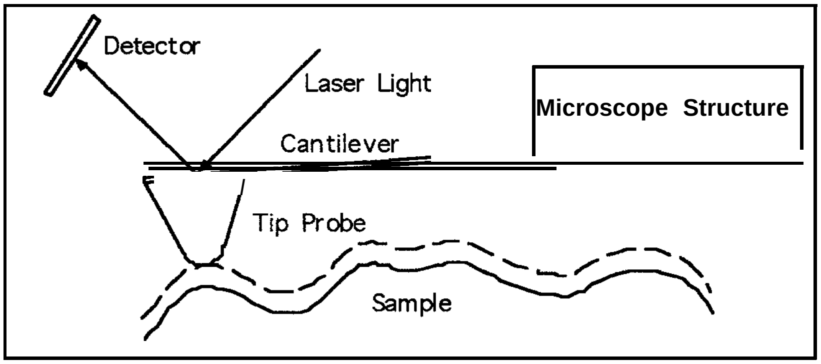

Figure 1: Schematic of the AFM.

One of the advantages of the AFM is that the technique works on insulators as well as conductors and is capable of routine nanometer resolution in ambient conditions. Moving the tip perpendicularly with respect to the sample surface provides data on the force of interaction between tip and sample and can, for example, provide information on the force of adhesion to a sample surface. The lateral force mode measures the forces on the tip cantilever parallel to the surface. This is a measure of the frictional forces between a probe tip and sample surface, making the AFM an ideal tool for tribological [9, 10] and wear [11] studies.

Scanning Tunneling Microscopy: Quantum mechanical tunneling of electrons through a classically forbidden energy barrier is exponentially sensitive to the barrier width, giving the scanning tunneling microscope (STM) unique three-dimensional atomic resolution [12]. The STM is schematically illustrated in Figure 2. A metal tip is brought within about 1 nm of the surface of a conductive sample. An applied voltage between the tip and sample establishes a small (on the order on nanoamps) but measurable tunnel current between the tip and sample. A feedback loop maintains a constant tunnel current as the tip is raster scanned *along* the surface. By recording the response of the feedback loop, an image of the surface is obtained. The tip-sample separation and raster scan are controlled by piezoelectric elements.

The interpretation of STM images is not always straightforward [13,14]. The tunnel current measured by the STM is not only proportional to the barrier width (given by the tip-sample separation) but also the local density of electronic states at the surface. Therefore, an STM image does not necessarily reflect only the topography of a surface. As AFM images should represent the actual topography of a surface (ignoring tip geometry artifacts), comparisons between AFM images and STM images have been made to check if a STM image has "electronic effect s" involved. An excellent example of this is the study of some high-temperature superconducting film[15]. Some of these sample (depending on their growth conditions) exhibited a surface made up of spiral structures superimposed on one another. It was determined by AFM images of the films that the relatively higher resolution STM images were indeed representative of the surface topography.

On a conducting sample, STM will generally provide superior resolution as compared to the AFM. In addition, the fact that the tunnel current is dependent on the local electronic density of states can be used to measure the spectra of electronic states near the Fermi level. In this mode, the tip is held at a point on the sample and the feedback loop is momentarily disabled. During this time, the voltage between the tip and sample is varied and the current response measured, thus measuring the current-voltage (I-V) characteristics of the tunnel junction between tip and sample. This is repeated to form an array of I-V characteristics over the sample surface; this technique is called scanning tunneling spectroscopy.

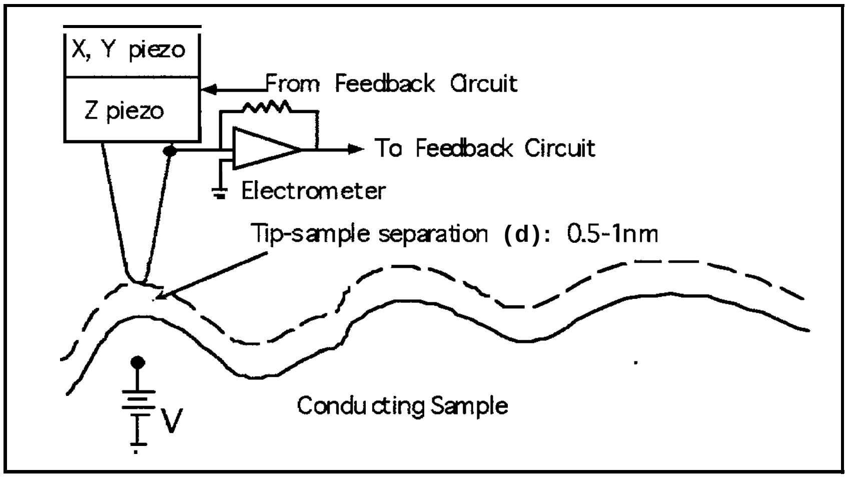

Figure 2: Schematic of the STM

Results and Discussion:

Preliminary data is shown below; Figure 3 shows an AFM image and Figure 4 shows a STM images of ilmenite surfaces. The AFM image is a 13 .4umx13 .4um scan. The sample was microscopically flat but the microscopic image reveals a fairly rough surface. The deep grooves evident in the image are likely due to the wafer polishing process. The overall surface roughness (in the large area on the left side of the image) is about 20-30nm. The STM image is a 1.5umx1.5um scan taken at a tunnel current of about 200pA at a junction bias of 3V. (Wide bandgap semiconductors are difficult to image with an STM because of their relatively high resistivity.) Microscopically the sample had few flat regions and appeared layered. The image was taken on a large (~3mm^2) flat area; the microstructure of this surface was characterized by parallel streaks. It is possible that the streaks in the STM image represent the layered crystallite structure (ilmenite has hexagonal crystal structure). The streaks in the STM image do not represent polishing artifact because this was not a polished sample. Being able to take STM data on ilmenite is encouraging because it holds the prospect of studying the density of states near the Fermi level with tunneling spectroscopy. The two images indicate about the same degree of overall surface roughness (20-30nm) for the "flat" region of the samples. However, given their relative scales, little more can be conclusively said about the two images. Work is in progress to further characterize ilmenite with these technique.

Conclusions:

- Ilmenite is a wide bandgap semiconductor with a variety of potential applications, including radiation resistant electronics.
- Scanning probe microcopies provide important information about the topography (AFM, STM) and electronic properties of a surface (STM).
- STM studies electronic properties of a conductive surface, while an AFM gives topographic information on both insulators and conductors.
- STM is possible on ilmenite, and thus tunneling spectroscopy.
- Additional SPM work is needed on ilmenite.

Acknowledgments:

This work is partially supported by the NASA/PVAMU Center for Applied Radiation Research and the Texas Advanced Technology Program. Data for Figure 3 was obtained by one of us (K. P.) at the Electron Microscopy Center of Texas A&M University.

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