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High Temperature Materials Synthesis Without Heat: Oxide Layer Growth on Electronic Materials Using High-Kinetic-Energy Atomic Oxygen

Mark A. Hoffbauer*, Jon B. Cross, and Frank A. Archuleta

Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). We examined thin-film materials-synthesis processes in which chemical reactions are initiated using high-kinetic-energy neutral atomic species instead of high temperatures. Our research is aimed at producing device-quality insulating oxide layers on semiconductor materials. Thick, uniform, and fully oxidized insulating layers of unprecedented quality are formed on gallium arsenide by exposure of wafer substrates to a high- kinetic-energy ($\sim 3\text{eV}$) neutral atomic-oxygen beam. The nonthermal oxidation process does not disrupt the crystalline order of the substrate and no detectable elemental arsenic is produced at the oxide/gallium arsenide interface.

1. Background and Research Objectives

Due to materials advantages, it is widely believed that GaAs-based compound semiconductors have the potential to replace silicon-based semiconductors in the next generation of electronic devices [1]. However, the intrinsic theoretical advantages of GaAs electronic devices over those employing Si technology are severely limited, in practice, by the difficulty of forming passivating oxide layers. In sharp contrast to the relative ease of forming insulating oxide layers on Si, severe problems are encountered with oxide stoichiometry, crystallinity, interface defects, and chemical stability on compound semiconductors, such as GaAs, that have been the subjects of numerous studies over the last 15 years [2-11]. One of the major factors contributing to these problems is the differing rates of thermal oxidation of Ga and As and the volatility of the As_2O_3 and As_2O_5 products at temperatures above $\sim 100^\circ\text{C}$. Over 15 years of intensive effort have totally failed to overcome the inherent difficulties in forming the required insulating and passivating oxide layers on GaAs.

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A wide variety of approaches to the growth of device-quality oxides at low temperatures on GaAs have been attempted [2-11]. Although, many of these techniques can greatly increase the rate of formation of the first few monolayers of oxide, they are generally unsuccessful in the growth of >20 Å-thick oxide layers. Further, the oxidation reactions do not result in Ga or As in their highest formal oxidation state, and the oxide is usually deficient in Ga or As and often contains excess metallic As.

The objective of this research project was to examine traditionally high-temperature materials synthesis, without using heat. While this may seem to be a contradiction in terms, the chemical synthesis processes we are investigating are initiated by high-kinetic-energy neutral species such as O atoms and N atoms. Because of their importance in the electronics industry, we placed particular emphasis on the direct growth of oxide and nitride insulating layers on semiconductor electronic materials such as GaAs. The ultimate goal of this research project is to use high-kinetic-energy neutral atomic species to directly produce device-quality insulating oxide or nitride layers on compound semiconductor materials.

2. Importance to LANL's Science and Technology Base and National R&D Needs

This research comprises an entirely new area of materials synthesis and chemistry that is totally unexplored, a direct consequence of the fact that high-kinetic-energy neutral atomic species are exceedingly difficult to produce. Los Alamos has a unique laser-sustained oxygen-atom beam facility that is capable of producing extremely high fluxes of atomic O (>100 monolayers/sec) at energies between 1 eV and 5 eV, and that has recently been shown to be capable of producing atomic N and H species. With this rare resource, unique opportunities exist for research in high-energy materials synthesis. Other experimental techniques are readily available for direct characterization of the substrate chemistry using in situ surface science spectroscopies, and for the detection of reaction products using mass spectroscopy and laser diagnostic techniques. Thus, the Los Alamos National Laboratory offers a unique combination of resources capable of understanding high-kinetic-energy materials synthesis.

New and revolutionary advances in electronic materials underlie the development of faster computers and advanced microelectronics for military and commercial applications. The fabrication of advanced semiconducting electronic devices and sensors has been identified as areas of strategic importance and future growth at the Laboratory. There should also be a great deal of interest in this novel process in a variety of other organizations in the U.S. and abroad. The implications of this process to space-based materials manufacturing technologies is also very apparent, and is an important consideration in accessing potential outside interest. We

have worked closely with SEMATECH, a consortium of U.S. semiconductor manufacturers, to identify applications of this technology to semiconductor manufacturing in the five to ten year time frame when current processes will be limited in their ability to produce the next generation of devices with smaller features and faster performance.

3. Scientific Approach and Results

Our experimental approach concentrated on investigating oxide layer growth on GaAs using a high-kinetic-energy beam source of neutral atomic oxygen. X-ray photoemission spectroscopy (XPS) [9], Raman spectroscopies [10], ATR infrared spectroscopy, X-ray diffraction, and photoluminescence measurements were used to characterize the thickness and stoichiometry of the oxide and to probe the oxide/GaAs interface.

Representative XPS data taken on the oxidized region of a GaAs substrate held at 50°C during the atomic oxygen exposure show the As 3d binding energy shift to be >4.5 eV. This result alone represents the formation of the most highly oxidized species ever observed on GaAs and may underscore the unique chemistry possible with the high-kinetic-energy atomic-oxygen beam.

XPS analysis and Ar⁺-ion sputter profiling have been performed to evaluate the composition and thickness of the oxide layer. The results indicate that the oxide layer has a nearly uniform chemical composition that we have tentatively identified as gallium arsenate (GaAsO₄), an assignment that is also supported by ATR/FTIR measurements. This represents the first observation of this chemical species in an oxide film. The oxide thickness is >200 Å for samples exposed at 50 °C and is significantly thicker for exposures at higher substrate temperatures (i.e. >400 Å at 150 °C). These observed oxide thickness are in the range required for the fabrication of electronic devices, and represent an improvement by at least one to two orders of magnitude over any known method of oxidizing GaAs substrates.

For oxidized III-V materials, Raman spectroscopy can be used to detect oxidation-induced disorder and the accumulation of the elemental column-V species at the oxide-substrate interface. Raman data for GaAs samples of various types with and without exposure to the atomic O beam have been measured. For the O-exposed surface, the results show that oxidation has not perturbed the crystalline order of the substrate to any measurable extent. This result stands in sharp contrast to over 15 years of other attempts to form oxide layers on GaAs [2-11].

Raman spectra of oxides grown by other processes on GaAs always show strong peaks associated with crystalline or amorphous As at the oxide/GaAs interface [10,11]. Oxide layers grown with our high-kinetic-energy atomic-oxygen source at 50 °C, 150 °C, and 280 °C

substrate temperatures show none of these features. Photoluminescence measurements, used to evaluate oxide quality, also show no degradation of the oxide/substrate interface. Thus, oxidation by high-kinetic-energy atomic oxygen does not produce metallic As in either the oxide layer or at the oxide/GaAs interface at moderate substrate temperatures. This is an absolutely necessary condition for the oxide layer to be considered device-quality.

We have demonstrated the formation of thick, uniform, and fully oxidized insulating layers on GaAs of unprecedented quality by exposure of GaAs wafer substrates to a high-kinetic-energy neutral atomic-oxygen beam. The oxidation process has no effect on the crystalline order of the substrate and results in no detectable (by Raman spectroscopy) levels of either crystalline or amorphous elemental As at the oxide-GaAs interface. These results definitely confirm that translationally-hot neutral atoms can be used to overcome many problems traditionally associated with the processing of compound semiconductor materials.

Additional experiments are required to establish the influence on the oxide layer formation kinetics of such processing parameters as sample temperature during O exposure, surface orientation, substrate carrier type and concentration, atomic oxygen beam kinetic energy and flux, and VUV radiation. A concerted effort is needed to identify the oxide species in the films and the influence of processing parameters on their formation. These parameters will be investigated in a follow-on effort to optimize the oxide thickness, growth rate, epitaxial structure, and electronic properties of the interface. In addition, current/voltage (CV) characterization of the oxide layer is being undertaken under well-controlled conditions with very careful substrate preparation in order to establish device quality and performance criteria for device production.

This LDRD project has concentrated on the oxidation of GaAs. Very recently, InP substrates have also been exposed to the atomic oxygen beam and are awaiting chemical analysis. Other compound semiconductor materials such as GaP, HgCdTe, etc., are known to also suffer from many of the same materials chemistry limitations as GaAs. These and other electronic materials may well be candidates for high-kinetic-energy growth of oxide layers.

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