

Rapid Deposition Technique Developed for High-Quality Metal Oxide Films

A method called laser-assisted molecular-beam deposition (LAMBD) has been developed by the AMBP Tech Corporation, in Amherst, N.Y. LAMBD creates uniform, high-purity thin films whose film growth can be controlled, with thicknesses ranging from a monolayer to several micrometers thick. These coatings all possess exceptionally flat, conformal morphologies. LAMBD is a high-temperature reactive process that simplifies the production of complex films such as metal oxide nitrides, carbides, and alloys. Metal oxides such as CeO_2 or HfO_2 are employed in the microelectronics industry for silicon-on-insulator (SOI) devices and also used to create buffer layers for superconducting tapes. LAMBD has advantages over other fabrication methods such as chemical vapor deposition (CVD), physical vapor deposition (PVD), and molecular-beam epitaxy (MBE). CVD offers high deposition rates, but often requires costly precursors and high temperatures and produces undesirable by-products. PVD and MBE, although relatively simple in principle, have deposition rates typically lower than CVD, and comparable film qualities cannot be achieved. In addition, many materials, such as oxides or insulators, cannot be efficiently deposited using conventional PVD and MBE techniques. In contrast, the LAMBD process can generate a wide variety of metal oxides with rapid deposition rates and the ability to directly control the growth of the film.

As in pulsed laser deposition, the LAMBD source uses an excimer laser to rapidly heat a pure metal target rod, generating a cloud of evaporated target material. However, PLD simply transfers an existing target material to a substrate. The LAMBD technique uses the laser pulse to chemically react a metal with oxygen gas

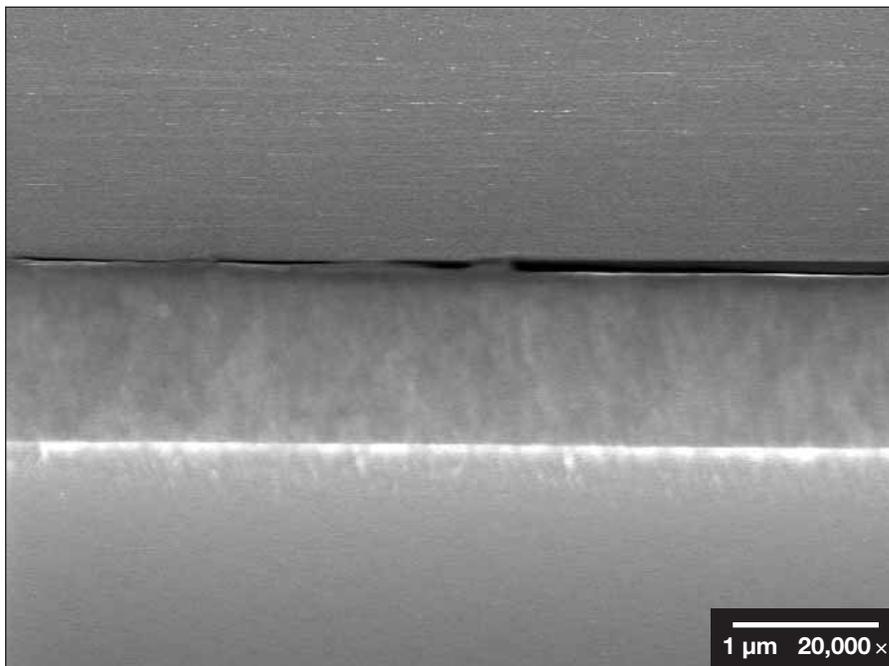


Figure 1. Edge view of a 1- μm thick hafnium oxide (HfO_2) film on silicon deposited by laser-assisted molecular-beam deposition (LAMBD).

to generate the metal oxide molecules. The resulting plasma of ablated metal atoms reaches temperatures as high as $15,000^\circ\text{C}$. A pulse of reagent gas, such as oxygen or nitrogen, is then injected into this cloud of vaporized material. The ablated metal target material and the gas pulse form a high-temperature chemical reactor. The reactions within this plasma occur with 100% efficiency, creating a stoichiometric product. For example, a titanium or gallium target rod can be used along with nitrogen gas to create titanium nitride or gallium nitride films; a Ce or Hf rod can be used with oxygen to generate cerium oxide (CeO_2) or hafnium oxide (HfO_2) films (i.e., high-dielectric-constant gate films). Multiple metal targets can also be used to create complex films or alloys.

The product molecules produced within the pressurized, external LAMBD source are expelled through a nozzle source into a vacuum deposition chamber, where they are simultaneously cooled and spray-deposited. With each pulse, a known amount of material is uniformly deposited onto the substrate. By adjusting the laser power and expansion conditions, the amount of material deposited by each pulse can be varied. Similarly, regulating the total number of pulses used in the deposition process allows precise control of the film thickness. Typical deposition rates are of the order of hundreds of

nanometers per minute. The resulting films are flat and both chemically and physically uniform, as shown in Figure 1.

Because the product materials are accelerated toward the substrate by the pressure differential between the LAMBD source and the deposition chamber, their kinetic energy levels are relatively low, reducing the potential for any substrate damage. This LAMBD technique can also be used to generate bulk quantities of nanoparticles by truncating the spray expansion with a stagnant buffer gas and then harvesting the resulting particles.

Opportunities

A prototype research and development system, with a 7.62-cm (3-in.) capability, has been developed and is ready to be commercialized. The LAMBD technique is scalable, and work is currently under way to coat 20.32-cm (8-in.) wafers and, later, 30.48-cm (12-in.) wafers. AMBP Tech Corp. is also interested in licensing this technology.

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Photoluminescence-Induced Metallization Forms Low-Resistance Contacts to Porous Silicon

There has been considerable interest in the development of compact and efficient devices from porous media, such as sensors for the detection of gaseous compounds important in environmental, food, and biomedical applications. To integrate sensor arrays with electronics, low-resistance electrical contacts are needed, requiring the development of techniques for the metallization of interface structures. Researchers at the Georgia Institute of Technology (Georgia Tech) have demonstrated the formation of a hybrid micro/nanoporous silicon-based structure whose photoluminescence (PL) can be greatly enhanced and stabilized by treatment with an aqueous HCl/methanol solution. This stabilized and enhanced PL, coupled with an electroless gold solution, produces a means for the PL-induced metallization of the PS interface resulting in contact resistances far lower than those typically associated with PS.

Porous silicon displays orange-red photoluminescence resulting primarily from a surface-based process tied to defect sites and the presence of surface-bound fluorophores (i.e., excited states of silicon oxyhydrides). However, the development of devices based on photoluminescence had been hindered by the need to enhance and stabilize the emission for a useful length of time and to obtain a low-resistance contact to the porous silicon. The researchers at Georgia Tech developed selective patterned metallization of porous silicon by using the photoluminescent surface as a reducing agent. The intimate environment associated with a controlled, photoluminescence-based, metallic-ion reduction is created from an electroless solution (i.e., plating without an electric current). This method uses the stabilized "long-lived" porous silicon luminescence to enhance reduction at the porous silicon surface.

The formation of surface-bound electronically excited "centers," whose interaction and reaction capability greatly exceed those of an unexcited surface, provides an enhanced and controllable reduction capability for electroless copper, silver, and gold solutions now used to achieve contact resistances in the 20–100- Ω range. The spreading resistances, which can exceed 10^4 – 10^6 Ω in a typical porous silicon sample, are prevented. In conventional electroless metal plating, the surface is usually coated first with palladium to catalyze the deposition

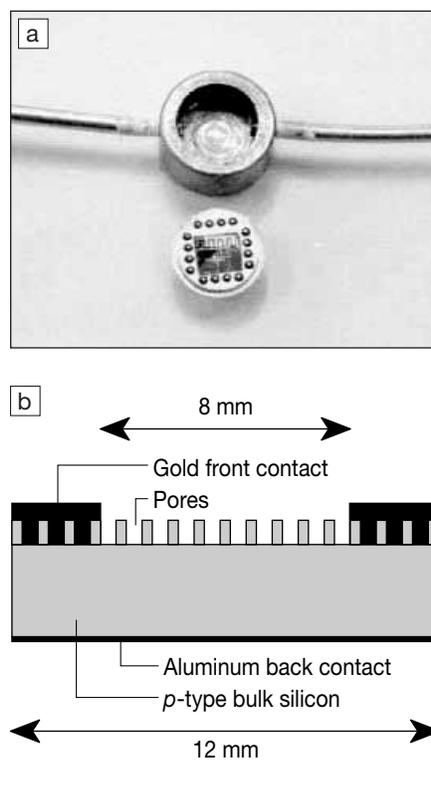


Figure 1. (a) Photograph of a porous silicon sensor and reaction flow chamber. Interdigitated electrodes can be observed. (b) Schematic cross-sectional diagram of a porous silicon sensor configuration, showing microporous-nanoporous array and photoluminescence-generated gold front contacts.

process. With the photoluminescence-induced approach, no catalyst is needed since the illuminated porous silicon surface itself catalyzes the deposition. Control experiments show that localized heating is not promoting the deposition reaction and that metal deposition occurs only when the porous silicon structure is illuminated at wavelengths consistent with the porous silicon bandgap.

A hybrid microporous-nanoporous silicon structure is employed for the electroless deposition. The pores are approximately 1 μm wide, between 3 μm and 8 μm deep, and covered with a thin nanoporous layer. After metallization, both the internal surface of the silicon pores and the surface of the silicon are coated, depending on the photoluminescence-induced region of deposition. The process subsequently quenches the photoluminescence in those areas where contact is established. In the absence of photoluminescence, no deposition occurs. A surface

that has been oxidized to silicon dioxide (SiO_2) or that does not photoluminesce, due to alternate quenching, does not plate metal. The low resistance suggests that porous silicon samples metallized in direct contact with the electroless solution experience minimal oxidation and form an excellent metallic contact to the porous silicon surface.

A sensitive conductometric porous silicon gas sensor (Figure 1), that uses photoluminescence-induced electroless metallization to obtain a highly efficient electrical contact, has been demonstrated for the detection of hydrogen chloride, ammonia, and nitric oxide at the 10-ppm level. The problem of spreading resistance ($k\Omega$ – $M\Omega$) is overcome since low-resistance contacts (~ 20 Ω) are made to the mesoporous silicon structure through electroless gold plating. The response of this device, which operates at a bias voltage of 1–10 mV, is rapid and reversible.

Possible applications of this photoluminescence-based metallization process, particularly in silicon-based systems, include the generation of magnetic pads (Ni, Co), and, based on a considerably enhanced contact, the development of highly efficient electrochromism-pumped photocatalytic interfaces. The simplicity of the process might be incorporated into the processing infrastructure for silicon integrated circuits. Integration of the electronic measuring system on chips might ultimately enable low-cost and easily mass-produced devices. The researchers are evaluating the electroless tin plating of the micro-nanoporous silicon structure with emphasis on the development of highly efficient Sn-Li alloy-based battery configurations. Similar electroless metallization techniques could be applied to the coating of derivatized silicon dioxide, tin oxide, and titanium oxide nanostructures as these structures are placed in porous silicon-based microporous arrays for sensor, catalyst, and battery applications.

Opportunities

Georgia Tech welcomes inquiries for licensing the technology and for partnering applications development.

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Intermediate HfN Layer Used to Grow GaN Film on Silicon

Gallium-nitride-based semiconductors have proven to be the preferred materials for applications in both short-wavelength optoelectronics (e.g., light-emitting diodes, laser diodes, and detectors in the green-UV range) and high-performance electronics (e.g., transistors for high-power, high-frequency, or high-temperature applications). GaN-based devices are typically fabricated from heteroepitaxial layers grown on sapphire or silicon carbide substrates. Replacing these substrate materials with Si would be advantageous because of considerable cost savings and the potential for monolithic integration of GaN-based devices with conventional microelectronics. Researchers at Lawrence Berkeley National Laboratory (LBNL) have shown that hafnium nitride (HfN) is an effective buffer layer for GaN film grown on Si.

Among the challenges that Si substrates present for GaN growth is that GaN is thermodynamically unstable with respect to silicon nitride (Si_3N_4), and Ga exhibits poor wetting on the Si surface. Therefore, low-temperature GaN—as typically employed on sapphire—cannot be grown directly on silicon without a buffer layer. High-quality GaN epilayers can be grown on Si using an aluminum nitride (AlN) buffer-layer process, which is the current technology in use. However, the mutual solubility of Si and Al is high at typical buffer-layer growth temperatures (~500°C). Therefore, AlN might exacerbate interdiffusion at the interface, leading to contamination of both the film and substrate. Additionally, the poor electrical conductivity of AlN hinders current flow to the device from back-side contacts made to the Si substrate. These limitations of AlN warrant the investigation of alternative buffer layers.

Films using HfN as a buffer layer exhibit epilayer quality comparable to the typical results achieved using AlN buffer layers. Epitaxial HfN films with smooth surfaces (<1 nm rms roughness) can be grown on Si by a sputtering deposition process. Furthermore, HfN has a nearly exact lattice match to GaN. Based on research from Si process technology, HfN offers excellent diffusion resistance. Unlike AlN, HfN is a metallic conductor, which forms an ohmic contact to *n*-type GaN. Thus, HfN buffer layers could enable the fabrication of devices such as metal-based transistors and provide built-in *n*-type contacts to facilitate the fabrication of conventional devices.

GaN epilayers ~1 μm thick grown on

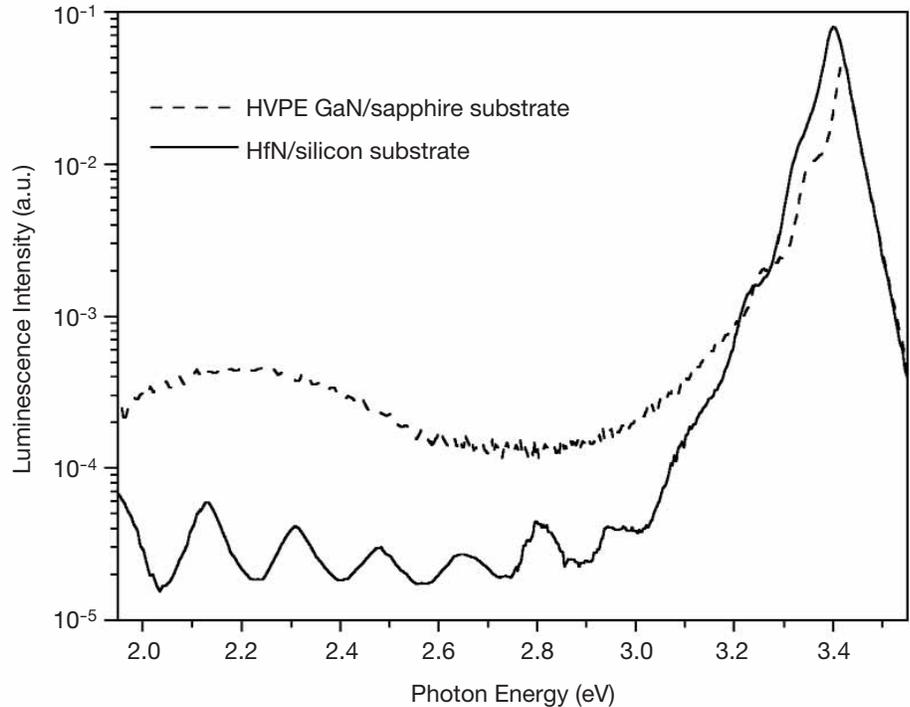


Figure 1. Room-temperature ($T = 295\text{ K}$) photoluminescence spectra for GaN grown on Si using a HfN buffer layer, compared with that of a reference sample grown by molecular-beam epitaxy on a GaN/sapphire template grown by hydride vapor-phase epitaxy (HVPE).

the HfN buffer layers using a standard rf plasma-assisted molecular-beam epitaxy (MBE) process exhibit mirror-like surfaces and structural quality similar to films grown on Si substrates using AlN buffer layers. The room-temperature luminescence spectrum for a representative GaN epilayer on HfN/Si 10-μm-thick compared to an MBE GaN film grown on sapphire (Figure 1) shows a comparable band-edge emission and a much weaker ~2.2-eV defect-related emission, indicating promising optical quality.

The band-edge luminescence peak shifts to lower energy for GaN grown on Si. This is due to the tensile stress arising from the difference in the thermal-expansion coefficients of GaN and Si. This stress often causes film cracking for thicker (>1 μm) layers. The largest GaN crack-free thickness demonstrated to date using the HfN/Si substrates is 1.2 μm. The HfN buffer layer does not offer any advantages over AlN with regard to the cracking problem. However, solutions such as strained-layer AlGaIn/GaN superlattices, previously implemented for growth on AlN/Si substrates, should also be applicable for HfN/Si substrates.

The HfN buffer layers were prepared at a process temperature of 450°C. Since

this is a very low temperature relative to the melting point of HfN (>3000°C), the films consequently have small lateral subgrain sizes of the order of 50 nm. A larger subgrain size in the HfN buffer layers is preferable for the overgrowth of GaN epilayers. Another parameter yet to be optimized is the HfN film thickness, which so far has been kept constant at 200 nm. Further improvements in GaN quality are expected with optimization of the HfN buffer layers.

Opportunities

Lawrence Berkeley National Laboratory is interested in licensing the technology and in collaborative research and development of HfN buffer-layer technology, particularly in optimizing the HfN deposition parameters and scaling up to production-scale sputtering systems.

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