

Pulsed laser deposition of lanthanum monosulfide thin films on silicon substrates*

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Thin films of lanthanum monosulfide (LaS) have been successfully deposited on Si substrates by pulsed laser deposition. The values of deposition parameters (chamber pressure, substrate temperature, substrate-to-target separation, laser energy, repetition rate, and spot size on the target) leading to a successful growth of films in their cubic rocksalt structure are identified. The films are golden yellow in appearance with a mirror-like surface morphology and possess a sheet resistance around $0.1 \Omega/\text{square}$. X-ray diffraction analysis of thick films (several microns) leads to a lattice constant of $5.863(7) \text{ \AA}$, which is close to the bulk LaS value. High-resolution transmission electron microscopy reveals the films to be comprised of nanocrystalline regions separated by amorphous ones. The root-mean-square variation of film surface roughness measured over a $1 \mu\text{m} \times 1 \mu\text{m}$ area is found to be 1.74 nm by atomic force microscopy. These films have potential for semiconductor, vacuum microelectronics, and optoelectronics applications. © 2005 American Vacuum Society. [DOI: 10.1116/1.1856477]

Rare-earth monosulfides with the rocksalt structure offer a more stable alternative than alkali metals to reach low or negative electron affinity (LEA/NEA) when deposited on various III-V semiconductor surfaces, as suggested by Mumford and Cahay several years ago.^{1,2} Of particular interest is the fact that the room temperature work function (WF) of these chalcogenides, when extrapolated from high-temperature measurements,³ is quite low (between 1 and 1.4 eV). One therefore expects that these materials can be used to reach NEA when deposited onto *p*-type semiconductors. For instance, bulk LaS has a lattice constant (5.857 \AA)⁴ very close to the lattice constant of indium phosphide (InP, 5.8688 \AA), and neodymium monosulfide (NdS) has a lattice constant (5.69 \AA) very close to the lattice constant of gallium arsenide (GaAs, 5.6533 \AA). Since the expected room temperature WF of LaS (1.14 eV) and NdS (1.36 eV) are, respectively, below the band gap of InP (1.35 eV) and GaAs (1.41 eV),⁵ NEA can therefore be reached at InP/LaS and GaAs/NdS interfaces using heavily *p*-type doped semiconductors. Two other important features of the rocksalt form of these rare-earth monosulfides are their fairly large melting temperature ($>2000 \text{ }^\circ\text{C}$) and their fairly low electrical resistivity (a few tens of $\mu\Omega \text{ cm}$). It is therefore expected that thin films of these compounds used to promote semiconductor surfaces to NEA should be stable and should not suffer from current crowding effects, which would lead to nonuniformity in the current emitted into vacuum.² Recently, we also pro-

posed an InP/CdS(cadmium sulfide)/LaS cold cathode based on the NEA at the CdS/LaS interface.¹

The feasibility to build the cold cathode structures listed above requires that thin films of high purity cubic LaS thin films be readily grown, and be lattice matched to III-V semiconductors. Recently, we have identified a process to successfully grow pure bulk LaS in the rocksalt phase.⁴ Furthermore, we were able to remove the oxysulfide impurity phase ($\text{La}_2\text{O}_2\text{S}$) generally present in LaS samples using a high-temperature carbon reduction process. The successful removal of the oxysulfide phase was supported by the absence of sharp phonon modes associated with this noncubic phase in Raman scattering experiments.⁴ In the past, several authors have reported the successful growth of LaS thin films using reactive planar magnetron sputtering,^{6,7} multi-source vapor deposition,⁸ and spray pyrolysis.⁹ In this article, we report the successful growth of LaS thin films using pulsed laser deposition (PLD).¹⁰ The films grown here are typically $1/2 \mu\text{m}$ to $1 \mu\text{m}$ thick. The investigation of these thicker films is a crucial step prior to growing thinner (a few monolayers thick) films of rare-earth sulfides as more stable alternatives to cesiated surfaces to reach NEA at the surface of III-V semiconductor compounds.

Using the carbon reduction process described in detail in Ref. 4, we first prepared a 2-in.-diam 3/8-in.-thick target, which was then used in a high-vacuum chamber (base pressure of 10^{-8} Torr) to deposit thin films of LaS by PLD. The quality of thin films grown by PLD is affected by several deposition parameters including: (1) substrate temperature, (2) laser repetition rate, (3) laser energy, (4) base and back-

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ground pressures, (5) substrate to target distance, and (6) the spot size of the laser beam on the target. The PLD system in our experiments is regularly used for growing tribological films for which optimal deposition parameters have been well established. We use these previous experimental results as an *ad hoc* approach to our first attempt to PLD of LaS films.

In our experimental setup, the target-to-substrate distance is 5 cm and the beam spot size on target is 1 mm by 3 mm. A Lambda Physik LPX 305 excimer laser operating at a wavelength of 248 nm was used for the deposition. The laser power was set to 800 mJ/pulse. Previous measurements have shown that approximately 56% of the laser energy is attenuated by the time the pulse reached the target due to losses from beam steering optics and the chamber window. Thus the amount of energy per pulse reaching the target is approximately 355 mJ/pulse.

During deposition, the target is rotated on axis while galvanometers are used to raster the laser beam in a uniformly random pattern over the surface of the target. This configuration produces a uniform laser plume by preventing uneven erosion of the target. A homogeneous laser plume is critical for producing films with uniform thickness.

The deposition chamber contains a rotating planetary substrate holder that can hold six substrates. Five can be shielded leaving only one substrate exposed to the laser plume allowing for the testing of different growth conditions for each film. Using a high laser repetition rate of 40 Hz allowed for six films to be grown in a reasonable amount of time (~2 h). All the films were grown on polished (100) silicon substrates with a base pressure in the chamber of 8×10^{-8} Torr. The silicon substrates were prepared using a standard cleaning procedure.¹¹ Each substrate was biased to 150 V, which accelerates the ionic species in the laser plume towards the substrate creating denser films.

Substrate temperature and background gas pressure were varied for each film growth to determine their effect on film quality. Initially the background gas pressure was varied between 10 and 30 mTorr of argon while the substrate temperature was set at 25, 100, 150, and 300 °C. Films grown above 100 °C were purple in color. Films grown at or below 100 °C appeared golden yellow as the bulk sample with a mirror-like surface morphology. The purplish color could be a combination of various effects including variation in film thickness resulting in a difference in the index of refraction of the films, variation in the film's composition and/or crystal structure. We speculate that the films grown at higher temperatures are sulfur deficient. Sulfur deficiency due to increased substrate temperature has been reported by several authors in experimental investigation of other sulfide films deposited by PLD or magnetron sputtering.¹²⁻¹⁴ This is consistent with the low sublimation temperature of sulfur. We only carried out a detailed characterization of the films that appeared golden in color after growth. An example of such a thin film grown over an area of 1 sq. in. is shown in Fig. 1. The film sheet resistance at room temperature was measured



Fig. 1. Photograph of a LaS thin film grown by PLD on a (100) Si substrate. The film appears golden yellow in color with a mirror-like surface morphology, as indicated by the reflection of a logo symbolizing our team effort. The PLD deposition is uniform over a 1 in. square area.

to be around $0.1 \Omega/\text{square}$ using a four-probe measurement technique.

A determination of the growth rate of the films was determined with the substrate temperature kept at 100 °C. These films were grown with no background gas pressure. Four films were grown with different deposition time of 5, 10, 20, and 30 min. The individual film thicknesses were then measured using a stylus profilometer. The deposition rate is found to vary linearly up to 10 min deposition time and a deviation from linearity appears to occur between the 10 and 15 min experimental data. Our last data point (30 min deposition time) seems to indicate a saturation in the film thickness for longer deposition time. Using the experimental data up to 10 min deposition time, the film growth rate is estimated at about 20 nm/min for this specific set of PLD parameters. The determination of the growth rate for short deposition times is an important parameter since the realization of the cold cathode structures described above would require deposition of just a few monolayers of the rare-earth monosulfides. The PLD process described here is therefore promising for the ability to grow very thin stoichiometric films since the amount of pulses needed to grow a film to a specific thickness can be determined. It is expected that a decrease in laser energy/pulse will result in a decrease in the deposition rate.

Figure 2 shows a typical x-ray diffraction (XRD) scan of a golden-yellow LaS thin film at a grazing angle ϕ from 1 to 3° using a RIGAKU D-2000 model XRD machine. The XRD scan shown in Fig. 2 reveals principal Bragg reflections of the cubic rocksalt phase. An analysis of the Bragg reflection peaks leads to a lattice parameters $a_o = 5.863(7) \text{ \AA}$, which is very close to the value we reported earlier for bulk samples, $a_o = 5.857(2) \text{ \AA}$.⁴ The observation of many Bragg reflection peaks suggests that the film is polycrystalline, which is to be expected because of the large lattice mismatch (about 8%) between the lattice constant of the LaS rocksalt phase and of

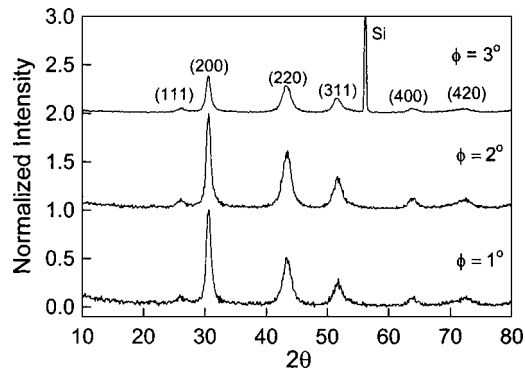


FIG. 2. X-ray diffraction at three different grazing angles of incidence (ϕ) from a LaS thin film deposited on a (100) Si substrate. Miller indices (hkl) of the reflections from the cubic rocksalt phase of LaS are identified. The peak located around 56° is due to the (311) Bragg reflection observed for a bare Si substrate (Joint Committee on Powder Diffraction Standard card No. 77-211).

the Si substrate ($a=5.431 \text{ \AA}$). Furthermore, the Bragg peaks are fairly broad suggesting the presence of polycrystalline grains of different sizes and potentially the presence of amorphous regions in the film. This was confirmed by cross-section transmission electron microscopy (TEM) analysis (Philips EM430T operated at 250 kV) of the LaS thin film and a representative high-resolution TEM lattice image is shown in Fig. 3(a). This image reveals the existence of randomly oriented nanocrystals and amorphous tissue in a proportion of approximately 60% to 40%, respectively. This is also illustrated in Fig. 3(b), which shows a blurry ring-like diffraction pattern from the LaS thin film. Two beam bright field TEM images ($g=400$) show that there is a strain contrast in the Si substrate right under the interface with the LaS film penetrating into the Si substrate. This suggests that there is an initial epitaxial-like growth of the LaS film on the Si substrate that introduces the strain as a result of the lattice mismatch between the film and substrate. Atomic force microscope scans of the LaS thin film over an area of $1 \mu\text{m} \times 1 \mu\text{m}$ revealed a root-mean-square variation in the surface roughness of 1.743 nm. This high smoothness of the film was verified over the entire area of the sample shown in Fig. 1.

Future work will be aimed at making more crystalline LaS thin films. A high substrate temperature with a background gas of H_2S and a slow deposition rate have proved to be optimal conditions for growing single crystal sulfide films.^{12,15,16} Currently, a PLD system is being built that will be dedicated to growing crystalline LaS thin films under optimal growth conditions.

In conclusion, we have reported the successful deposition of lanthanum monosulfide (LaS) thin films in their cubic rocksalt phase by PLD on Si substrates. The use of PLD to deposit other rare-earth sulfides on a wide variety of substrates is now under investigation. These rare-earth sulfide thin films should have potential applications in vacuum microelectronics if they can be used to reach NEA/LEA at the surface of various III-V and II-VI compound semiconductors. Applications would include microwave vacuum transis-

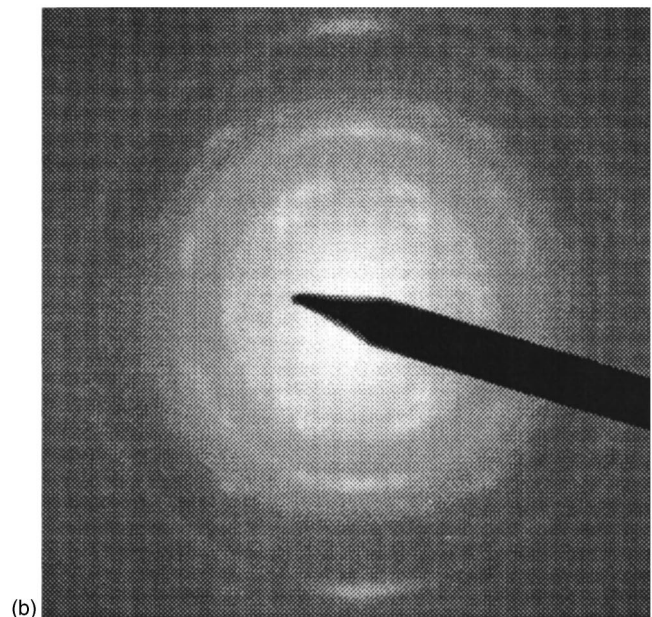
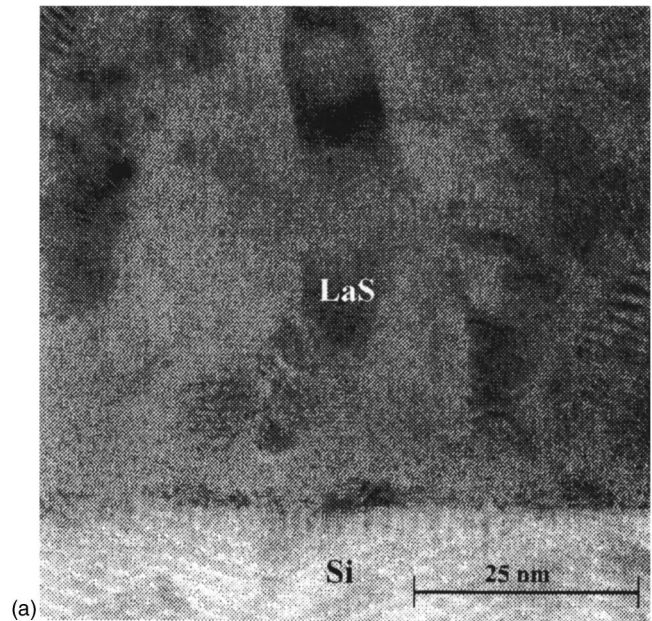


FIG. 3. (a) High-resolution TEM image of the LaS/Si interface for a $1\text{-}\mu\text{m}$ -thick LaS film grown on a (100) Si substrate. Despite the large lattice mismatch between the two materials, the interface is rather smooth at the length scale shown in this TEM picture. (b) The blurry-ring diffraction pattern of the LaS film reflects the coexistence of nanocrystalline and amorphous phases, which can be clearly identified from the presence or absence of lattice fringes in Fig. 3(a). The bright diffraction spots arise from the Si substrate.

tors and tubes, pressure sensors, thin panel displays, and high-temperature and radiation tolerant sensors. Also, the low WF of rare-earth monosulfides and their chemical and thermal stability make them perfect candidates as cathode materials to build reliable and durable organic light-emitting diodes. The PLD technique could also be extended to thin films of other rare-earth chalcogenides (like LaSe) which have potential applications in switching, photoconductive, and thermoelectric devices.¹⁷

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