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Field emission from lanthanum monosulfide thin films grown on the (100) magnesium oxide substrates

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Lanthanum monosulfide (LaS) films were grown by pulsed laser deposition on the (100) magnesium oxide (MgO) substrates at an elevated substrate temperature and in a background gas of H₂S. The thin films have been characterized by x-ray diffraction (XRD), atomic force microscopy (AFM), and high resolution transmission electron microscopy. The film surface is composed of grainlike features with an average size of approximately 34 nm. The root-mean-square variation of the film surface roughness measured over a $2 \times 2 \mu\text{m}^2$ area by AFM was found to be approximately 1.5 nm. XRD data indicate that the average size of the nanocrystalline grains in the film is about 26 nm, which is about twice the size of the grains found in LaS thin films deposited at room temperature on Si. The field emission (FE) properties of the films have been characterized by scanning anode field emission microscopy and are interpreted in terms of a recently developed patchwork FE model. The FE data indicate that there is roughly a seven times increase in emission area due to the (100) patch areas outcropping the surface for LaS/MgO compared to LaS/Si thin films. © 2008 American Vacuum Society. [DOI: 10.1116/1.2837909]

I. INTRODUCTION

Recently, we have reported the successful growth by pulsed laser deposition (PLD) of nanocrystalline LaS thin films on Si (100) substrates at room temperature.^{1,2} The films are golden yellow in appearance with a mirrorlike surface morphology and a sheet resistance of around $0.1 \Omega/\text{sq}$, as measured using a four-probe measurement technique. The root-mean-square variation of the surface roughness of the approximately $1 \mu\text{m}$ thick film measured over a $1 \mu\text{m}^2$ area by atomic force microscopy (AFM) was found to be 1.74 nm. x-ray diffraction (XRD) analysis of this film revealed the successful growth of the cubic rocksalt structure with a lattice constant of $5.863(7) \text{ \AA}$, which is close to the bulk LaS bulk value of $a=5.857(2) \text{ \AA}$.³ The x-ray peaks were very broad indicating a poor degree of crystallinity. High resolution transmission electron microscopy (HRTEM) images showed the films to be mainly amorphous with crystalline regions consisting of small grains separated by re-

gions of amorphous material. The amorphous and crystalline regions comprised approximately 60% and 40% of the film, respectively.^{1,2}

Field emission (FE) measurements from these LaS planar cathodes were interpreted based on a patchwork distribution of the work function of the surface. Nanocrystals having a (100) orientation perpendicular to the surface and outcropping it are believed to be responsible for the low work function of 1.05 eV recorded using the scanning anode field emission microscopy (SAFEM) technique. Very recently, the FE data were interpreted using a self-consistent FE model from the (100) areas having a mean size of 5 nm, with an effective work function of 1.05 eV and covering 1/1000th of the entire surface.⁴

The goal of this research was to prepare crystalline, epitaxial films of LaS with the (100) orientation capable of delivering higher emission current density than reported for the largely amorphous LaS/Si thin films. The approach is based on PLD at high temperature in a background gas of H₂S following the work of Piqué *et al.*^{5,6} Single crystal MgO (100) with the NaCl structure was selected as the substrate of

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choice: MgO has a lattice constant of 4.213 Å. Cubic LaS has a lattice constant of 5.857 Å (Refs. 3 and 7) leading to a lattice mismatch of 1.69% when aligned with the unit cell diagonal of MgO (5.957 Å).

II. EXPERIMENTS

The LaS films were grown on polished (100) MgO substrates which were prepared using a standard cleaning procedure. In the PLD experimental setup,^{1,2} the target to substrate distance was 12 cm and the vacuum chamber base pressure was 3×10^{-9} Torr. A pulsed Lambda Physik LPX 305 excimer laser operating at a wavelength of 248 nm and a repetition rate of 4 Hz was used for the deposition. The beam spot size on target was 4×8 mm² and the laser energy on target was 320 mJ/pulse corresponding to a fluence of 1 J/cm². During deposition, the target was rotated on axis while galvanometers were used to raster the laser beam in a random pattern over the target to prevent uneven erosion of the target surface.

XRD θ - 2θ scans were performed using a PanAlytical X'Pert Pro x-ray diffraction system in which the incident angle was set equal to 5°. Surface images were obtained by AFM using a Pacific Nanotechnology Nano-R SPM, model No. 0-200-002 operating in vibrating mode. Line scans were performed to measure the surface roughness and grain size of the films.

To investigate the crystalline texture of the films, cross-sectional transmission electron microscopy (TEM) samples were prepared following standard procedures. Two bars were cut out of a wafer and were glued together with the LaS film sides face to face to make the central part of the 3 mm diameter cross-sectional sample disk. The disk was then mechanically thinned to ~ 100 μ m thickness. The thinned disk was dimpled from both sides with 3 μ m diamond paste until the center of the disk was ~ 20 μ m thick, and then polished from both sides with 1 μ m diamond paste to get a very smooth surface. The final thinning to produce sample perforation was conducted using Ar ion milling from both sides with an ion beam angle of 9°, and a gun voltage of 6 kV. The TEM sample was examined in a JEOL JEM-2100F field emission source microscope operating at 200 kV.

The SAFEM technique was used to measure the current-voltage (I - V) characteristics at different surface locations and at different temperatures of a LaS thin film with an area of about a 1 cm².^{8,9} For one location, the full set of measured I - V characteristics (total measured current versus applied voltage) for different values of d , the distance between the cathode surface and the probe ball, were then analyzed in order to extract the current density J versus actual applied field F (J - F) data.

III. EXPERIMENTAL RESULTS

A. PLD experiments

A very thorough investigation of LaS thin films was conducted in order to study the granularity and texture of the films as a function of the substrate temperature, laser repetition

rate, and H₂S background gas pressure.¹⁰ It was found that a substrate temperature of at least 400 °C coupled with a low laser repetition rate and at least 20 mTorr of H₂S were needed to produce crystalline, cubic LaS as evidenced by XRD. The sample used for this field emission experiment was grown at 400 °C in 24 mTorr of H₂S with a laser repetition rate of 4 Hz for 30 min. HRTEM measurements revealed the resulting film thickness to be about 135 nm, corresponding to a deposition rate of 4.5 nm/min. The film was golden yellow in appearance with a mirrorlike surface morphology which is indicative of a successful growth of the cubic rocksalt phase of LaS.^{1,2}

B. XRD results

The bottom scan in Fig. 1 shows the XRD scan of the golden-yellow LaS/MgO thin film grown under the deposition conditions mentioned above. The scan reveals principal Bragg reflections of the cubic rocksalt phase of LaS in good agreement with those we reported earlier for bulk LaS as well as LaS thin films grown on silicon substrates.¹⁻³ The XRD (111) and (311) peaks (at 26.34° and 51.74°, respectively) are relatively much smaller in amplitude than the ones observed in the XRD pattern of LaS/Si thin films.^{1,2} This is indicative of enhanced conditions for epitaxial growth by using MgO substrates at an elevated temperature. The smaller peaks around $2\theta \sim 38^\circ$ and 45° are indicative of small amounts of La₂O₂S, LaS₂, and La₂S₃ impurity phases in the film.

Since the (200) peak is the most prominent in all of the XRD patterns, it was used to calculate the LaS lattice constant. This leads to a lattice constant $a = 5.868(2)$ Å which is just 0.19% larger than the 5.857(2) Å value reported for bulk samples.³ The (200) Bragg reflection peak has a full width at half maximum (FWHM) of 0.32° which is much narrower than the one measured for LaS thin films grown on silicon.^{1,2} An XRD scan for a LaS/Si thin film is shown in the top scan in Fig. 1. This film was also grown at a 4 Hz laser repetition rate, however, it was grown at room temperature in vacuum with no added H₂S. The narrower width of the Bragg peaks in the LaS/MgO sample also suggests a reduced amorphous content and an improved epitaxial nature for this film, as confirmed by the HRTEM images shown below. Using Scherrer's equation,^{11,12} the size of the nanocrystalline grains in the LaS/MgO thin film can be estimated from the FWHM of the (200) Bragg peak while taking into account a line-width correction for x-ray instrumentation broadening. Starting with the (200) Bragg peak in Fig. 1 and using $\lambda = 1.541$ Å for the wavelength of the Cu $K\alpha$ line, the average size of the nanocrystalline grains is found to be about 26 nm, which is about twice the size of the grains measured in LaS/Si thin film deposited at room temperature.^{1,2} This estimate agrees well with cross-sectional TEM analysis of the LaS/MgO thin film, as described below.

FIG. 1. (Top) θ - 2θ XRD scan of a LaS/Si thin film grown using the same PLD parameters as for the LaS/MgO thin film, except that the Si substrate was held at room temperature and no H₂S background gas was used during the growth. (Bottom) θ - 2θ XRD scan of a LaS thin film deposited on a (100) MgO substrate. Miller indices (*hkl*) of the most predominant reflection peaks from the cubic rocksalt phase of LaS are identified. Smaller peaks corresponding to La₂S₃, LaS₂, and La₂O₂S impurity phases are also indicated.

C. AFM results

Figure 2(a) shows an AFM image of a LaS/MgO sample over a $2 \times 2 \mu\text{m}^2$ area. The root-mean-square (rms) variation in the surface roughness was found to be 1.5 nm. For comparison, Fig. 2(b) shows an AFM image of a LaS/Si sample over a $2 \times 2 \mu\text{m}^2$ area grown using the same PLD parameters and no H₂S background gas with the substrate held at room temperature. Figure 2(b) indicates that this film is much smoother with a rms variation in the surface roughness equal to 1.13 Å. The difference in the AFM scans between the two films with an abundance of grainlike features in the LaS/MgO thin films leads to an enhanced field emission properties for these films, as discussed below. The grainlike features in the LaS/MgO film is illustrated in Fig. 3 which

shows different AFM line scans taken at different locations in the sample. From these line scans, the average size of the grainlike features on the surface is estimated to be about 34 nm. These grains are polycrystalline as revealed by HRTEM experiments.

D. HRTEM results

Figure 4 shows a HRTEM image of the sample grown on MgO at 400 °C in 24 mTorr H₂S at a laser repetition rate of 4 Hz for 30 min. This image shows a film thickness of approximately 135 nm corresponding to a deposition rate of approximately 4.5 nm/min. Figure 5 is a HRTEM image of the LaS film interface with the MgO substrate. The arrows indicate areas where nanocrystalline growth is occurring.

(a) LaS/MgO **(b) LaS/Si**

FIG. 3. Three different line scans obtained from the AFM data of a LaS/MgO thin film shown in Fig. 2(a). The average grainlike feature size on the surface is estimated to be about 34 nm.

FIG. 2. AFM scans over a $2 \times 2 \mu\text{m}^2$ area of (a) a LaS thin film grown on a (100) MgO substrate and (b) a LaS thin film grown on a (100) Si substrate. The PLD parameters for both films were identical, except that the Si substrate was held at room temperature and no H_2S background gas was used during the growth.

Figure 6 is a HRTEM image of the film just above the interface. The film has become polycrystalline in this region, consisting of small grains with different crystallographic orientations. Figure 7 shows a HRTEM image of the middle of the film with several regions showing significant amounts of atomic ordering. Fairly large crystalline grains can be seen as indicated by the white arrows. Finally, Fig. 8 shows a

FIG. 4. HRTEM image of a LaS thin film grown on a MgO substrate. The film thickness is about 135 nm.

FIG. 5. HRTEM image of the LaS/MgO interface.

FIG. 8. HRTEM image of the top surface of the LaS thin film.

FIG. 6. HRTEM image of the LaS thin film in a region just above the LaS/MgO interface.

FIG. 7. HRTEM image in the middle of the 135 nm thick LaS thin film.

HRTEM image near the top of the film, which also contains fairly large crystalline grains indicated by the arrows.

E. FE characteristics

The SAFEM technique was used to measure the FE current-voltage (I - V) characteristics at different surface locations. For each surface location, a full set of I - V characteristics (total measured current versus applied voltage) was recorded for different values of d . Typical experimental results are shown in Fig. 9. For LaS/MgO and LaS/Si cathodes, the maximum emission current was kept under ~ 1 and $\sim 0.1 \mu\text{A}$ for LaS/MgO and LaS/Si cathodes, respectively, which is well below the emission where the burnout regime of operation occurs, as described in detail in Ref. 4. The burnout regime occurs at emission current values of the order of 40 and $2 \mu\text{A}$ for LaS/MgO and LaS/Si cathodes, respectively. These low currents were used to prevent destruction of the surface of the cathode, to keep the I - V characteristic measurements reversible, and to allow multiple I - V measurements at different anode to cathode distances on the same spot on the surface. Under these conditions, the FE charac-

FIG. 9. Experimental FE characteristics of planar LaS/MgO and LaS/Si cathodes. Each of these plots represents an average over four or five different measurements at the same point and for the same distance d . The total emission current I for different V values depend strongly on the distance d (3.6 and $4.4 \mu\text{m}$) between the probe ball and the cathode surface.

FIG. 10. FE characteristics of planar LaS/MgO and LaS/Si cathodes. To allow comparison, the FE characteristics are plotted using the current densities vs local electric fields obtained from a set of I - V at different distance d and an analysis presented in Ref. 8.

teristics were reproducible. However, Fig. 9 shows that, for a given emission area, the I - V plots depend strongly on the distance d , making it therefore very difficult to perform a comparative analysis of the experimental data. The main reason for this effect is that the active field emission area under the probe ball and the variation of the local electric field across this area vary for different values of d , due to the hemispherical geometry of the probe.

To overcome this problem, an analytical extraction of the corresponding current density versus local electric field based on numerical simulations has been proposed and this analysis was presented in Ref. 8. For this analysis, the potential distribution between the cathode surface and the probe ball were calculated using a full set of I - V characteristics for different values of the probe to sample surface distance, d . Using this technique, the experimental results for FE from LaS/MgO cathodes can be compared to their LaS/Si counterparts, as shown in Fig. 10. Due to the patch emission process, only part of the actual cathode surface is active in field emission. Subsequently, we have introduced a parameter α which is the ratio between the active emitting area and the total cathode surface area under the probe ball. Therefore, the apparent current density is αJ , with J the notional FE current density from the active emitting zone. For LaS patchwork cathodes, α means the apparent ratio of outcropping low work function (100) zones to the total cathode surface and J is the actual current density extracted from these (100) zones (Fig. 11). Within this provision, the (I - V) measurement set was then analyzed in order to extract the apparent current density αJ versus actual applied local field γF , where γ is the local geometrical field enhancement at the surface of the cathode, and F is the notional electric field at the corresponding flat LaS cathode surface (i.e., when $\gamma=1$).¹³ We assume a γ value of 1 for both LaS/MgO and LaS/Si cathodes even though the roughness of the LaS/MgO surface is greater than for the LaS/Si surface. This assumption is justified by the geometry of the protrusions responsible for the surface roughness, as shown in Fig.

FIG. 11. Schematic of the patchwork model of the cathode surface. The emitting areas are preferentially limited to the outcropping (100) areas of the LaS nanocrystals which have a work function in the range of 1 eV.

3. The protrusions are in the range of 0.5 nm in height and a base diameter of about 40 nm for LaS/MgO, and for such values of protrusion geometry, the field enhancement factor is negligible.¹⁴

The purpose of the following field emission analysis is to determine if the increase in the nanocrystal dimensions has any consequence in the field emission properties of the LaS/MgO cathode. We adopt for such an approach a comparative analysis with experimental results obtained with LaS/Si and with theoretical data obtained from numerical simulations from a uniform cathode. The assumptions used are (i) the corrugations of the LaS/MgO and LaS/Si surfaces are small, therefore the field enhancement factor $\gamma=1$; (ii) for growth on either MgO or Si, LaS thin film surfaces present a patchwork distribution of the work function, with a value of 1.05 eV for nanocrystals having a (100) orientation perpendicular to the surface area and outcropping it. The ratio between the (100) surface area and the total cathode surface area is quantified by the factor α . In order to determine this factor α , we have performed a numerical fit between the experimental data and the theoretical J - F result for a uniform 1.05 eV cathode. The results are presented in Fig. 12 and they show that for LaS/MgO, a value of $\alpha=1/150$ gives a good fit; whereas for LaS/Si the fit gives a value of $\alpha=1/1000$. Practically, these results mean that for LaS/MgO the (100) patch emission area is 1/150 of the probe area; and that it is $(1000/150)=6.7$ times larger than the FE area of the

FIG. 12. Fowler-Nordheim plot of FE of a LaS/Si and LaS/MgO planar cathode. Also shown are the results of numerical simulations for a full area emitting cathode (Ref. 15).

LaS/Si sample. This increased FE current correlates well with the increase in grain size on the surface by changing the substrate from Si to MgO. TEM images of the LaS/Si surface show nanocrystalline regions on the order of 5 nm surrounded by amorphous regions,² whereas AFM revealed an average grain size of 34 nm on the surface of the LaS/MgO sample with a much higher density of crystalline regions at the surface. Considering that the (100) patch density for the LaS/MgO sample is only ~15% of the LaS/Si sample, the FE data indicate that there is roughly a seven times increase in emission area due to the (100) patch areas outcropping the surface for LaS/MgO compared to LaS/Si thin films.

IV. CONCLUSIONS

LaS thin films were grown by PLD on the (100) MgO substrates at an elevated substrate temperature and in a background gas of H₂S. The surface of the LaS/MgO thin film was composed of grains with an average size of approximately 34 nm. XRD data indicate that the average size of the nanocrystalline grains within the film is approximately 26 nm, which is about twice the size of the grains measured in LaS thin films deposited at room temperature on Si. The FE properties of the films have been characterized by SAFEM and successfully interpreted in terms of a recently developed patchwork FE model,^{4,9} in which the LaS surface presents a patchwork distribution of the WF with a value of 1.05 eV for nanocrystals having a (100) orientation perpendicular to the surface and outcropping it. The FE data indicate that there is roughly a seven times increase in emission area due to the (100) patch areas outcropping the surface for LaS/MgO compared to LaS/Si thin films. Future work will focus on optimizing the size of the LaS nanocrystals in order to determine the main parameters influencing the formation of a patchwork cathode.¹⁵ The smallest effective work func-

tion surface will be sought by tuning the PLD parameters to create the optimum size for the outcropping (100) nanocrystals. This could lead to the possibility of developing large emission area cathodes by tailoring the substrate geometry in order to establish a new rare-earth monosulfide cold cathode technology leading to very stable and large total FE currents at low applied voltage.

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