Deposition of lanthanum sulfide thin films by atomic layer epitaxy

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Abstract

Lanthanum sulfide thin films prepared using atomic layer epitaxy technique were analysed by X-ray diffraction and X-ray photoelectron spectrometry. The films grown from a β-diketonate precursor and H_2S were amorphous below 400°C. The first traces of crystallization appeared above 400°C, and at 500°C films of well-defined cubic γ-La_2S_3 structure could be deposited. XPS analysis revealed the presence of La_2S_3 both in amorphous and crystallized samples. Upon annealing at 510–730°C the material reacted with residual oxygen in the bulk and La_2O_2S and other oxysulfides were formed.   © 1998 Elsevier Science S.A.

Keywords: Lanthanum sulfide; Lanthanum oxysulfide; Thin film; Atomic layer epitaxy; X-ray photoelectron spectroscopy

1. Introduction

Materials for infrared and window applications transmitting in the IR region (8–14 μm) are limited to diamond, ZnS (or ZnS/ZnSe), $CaLa_2S_4$-type ternary sulfides and La_2S_3 [1]. Lanthanum sesquisulfide, besides having the widest transmission range (0.5–14 μm), possesses a suitable combination of low thermal expansion coefficient, high melting point and sufficient mechanical hardness, making it an attractive alternative for future IR applications. La_2S_3 exists in two crystalline modifications: the low temperature form (α) is orthorhombic while the cubic phase (γ) can be prepared at temperatures above 1000°C [2]. The intermediate tetragonal phase (β) is in reality an oxysulfide ($La_{10}S_{15-x}O_x$) where a part of the sulfur is replaced by oxygen [3]. The β-phase appears to be not as fully characterized as the other known oxysulfides, $La_{10}S_{14}O$, $La_2O_2S_2$ and La_2O_2S [3,4]. La_2O_2S is also an excellent optical host lattice, transparent in the range from ultraviolet to far infrared region [3]. Furthermore, La_2O_2S is also recognized as a host matrix material for cathodoluminescent phosphors [5].

γ-La_2S_3 has a defective cubic Th_3P_4 structure similar to $CaLa_2S_4$ [6]. It has been prepared and studied for optical purposes so far only as bulk material [1,2,7]. The corresponding Ce_2S_3 phase is isostructural with La_2S_3, displaying intense color which makes it a potential new pigment

to replace the toxic cadmium sulfo-selenides in plastics [8]. Our interest in (γ-)La_2S_3 thin films stems from the studies on PbS for IR detectors [9,10] where a protective and IR-transmissive layer is needed to seal the PbS thin film from the environment. Also the possible formation of oxysulfide phases is of interest.

Here we report on the novel possibility to prepare lanthanum sulfide thin films at a relatively low temperature using the atomic layer epitaxy (ALE) technique. ALE is a digital chemical vapour deposition method where the substrate surface is alternately exposed to the fluxes of evaporized anion and cation precursors [11]. In an ideal process, the film grows via cycles of saturated surface reactions in a self-controlled manner.

2. Experimental

Lanthanum sulfide films were grown onto 5×5-cm^2 Corning 7059 or soda lime substrates using a hot-wall flow-type ALE reactor (Microchemistry Ltd., Espoo, Finland) [11]. Nitrogen (purity 99.999%) was used as a carrier and purging gas. The primary N_2 flow was 0.3 dm^3 min^{-1}. The total pressure in the reactor was around 2 mbar, measured from the evacuation line. La(thd)$_3$ (thd= 2,2,6,6,-tetramethyl-3,5-heptanedione) synthesized by us, was evaporated from open boat placed in the inlet tube before reaction zone. Evaporation temperature was varied from 127 to 180°C. Temperature in the reaction zone was varied between 300 and 500°C. The pulsing of the metal precursors was accomplished by means of inert gas valving

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[11]. H_2S (purity 99.999%) was led into the reactor through needle and solenoid valves from an external reservoir held at room temperature. The flow rate of H_2S was 10^{-2} dm^3 min^{-1}. The pulsing times were in the order of 1 s.

Transmittance spectra of the films deposited onto bare glass and substrates supplied with ion barrier (Al_2O_3) layer were measured within a wavelength range of 370–1100 nm using a Hitachi U-2000 spectrophotometer. A fitting method developed and described by Ylilammi and Ranta-aho [12] was exploited for evaluating film thicknesses and refractive indices from these spectra.

A few selected samples were heat-treated in a rapid thermal annealing furnace PEO 601. The annealing procedure was carried out in nitrogen atmosphere during 1–4 h at 510, 630 or 730°C. The crystallinity of the as-deposited and annealed lanthanum sulfide films was examined with a Philips MPD 1880 powder X-ray diffractometer using Cu Kα radiation.

X-ray photoelectron spectroscopy (XPS) was used to study the contamination level and the chemical state of the lanthanum sulfide films. The measurements were performed with a Kratos Analytical AXIS 165 spectrometer using monochromated Al Kα radiation, 0.5 eV step and 80 eV analyser pass energy. For the analysis, samples were cut into 5×5-mm^2 pieces, mounted on a sample holder with UHV tape and evacuated. As samples were insulating, neutralisation of the sample surface with slow electrons during the data acquisition was utilised. Slight charge overcompensation resulted in a constant -2 eV shift in the measured binding energies. For some samples, depth profiling was carried out using argon ions (4.5 kV, 20 mA).

3. Results and discussion

3.1. Influence of deposition parameters.

The lanthanum sulfide films exhibited considerable thickness profile regardless of deposition parameters. The film thickness was the highest at the leading edge of the substrate array and then decreased by approximately 50% along the gas flow direction towards the trailing edge.

Thermal behaviour of the La(thd)$_3$ precursor has been studied earlier in connection of LaNiO$_3$ deposition [13]. Here the influence of the La(thd)$_3$ evaporation temperature and cycle time parameters was studied at a growth temperature of 380°C. An increase in source temperature from 127 to 155°C increased the growth rate at the leading edge of substrate as did the combined increase of La precursor exposure time and H_2S pulse duration. When H_2S pulses longer than 2 s were used, the growth rate stabilized at about 0.015 nm cycle^{-1} as measured at 4 and 6 cm from the leading edge of the substrate. On the other hand, the prolongation of the purge time after H_2S exposure resulted in a reduced growth rate by 25%,

approximately. An analogous decrease in growth rate can be observed, for instance, in the ALE deposition process of oxide films [14] and could be explained with thermal desorption or(and) reconstruction of the favoured adsorption sites before subsequently arriving precursor pulse.

As expected, the film growth rate was dominantly determined by the deposition temperature (Fig. 1). In the approximate temperature range of 360–410°C, a narrow plateau (ALE-window) with nearly temperature-independent growth rate of 0.015 nm cycle^{-1} can be observed. The film growth rate increases rapidly above 425°C and the thick films obtained at temperatures above 450°C possessed dark brownish colour indicative of precursor decomposition and uncontrolled CVD-type growth. These deposition temperatures used here are much below those reported in the literature where conventionally the γ-phase has been prepared at 1000–1200°C [1,2,7]. Recently, however, Roméro et al. have developed a process where the γ-phase can be prepared starting from rare earth oxalates and carbon disulfide even at 800°C [15].

The refractive index of lanthanum sulfide films at $\lambda = 580$ nm was determined from transmittance spectra and its value reached 2.70–2.75, being somewhat dependent on growth temperature. This value is in agreement with that reported for single crystal γ-La$_2$S$_3$ (2.6–2.8) and significantly higher than the bulk value measured for La$_2$O$_2$S (2.2) [3].

3.2. Film structure and composition

3.2.1. X-ray diffraction

Films grown at 380°C were amorphous as determined by XRD measurements. Some crystallization appeared above 400°C, regardless of the substrate used. In an attempt to obtain in situ the crystalline La$_2$S$_3$ phase, depositions were also carried out outside the ALE-window, that is above 425°C. At 500°C, crystalline material was obtained (Fig. 2) which was identified as the γ-phase of La$_2$S$_3$ [16].

Amorphous lanthanum sulfide films deposited at 380–500°C crystallised after annealing (Figs. 3 and 4). The extent and character of crystallization was dependent on
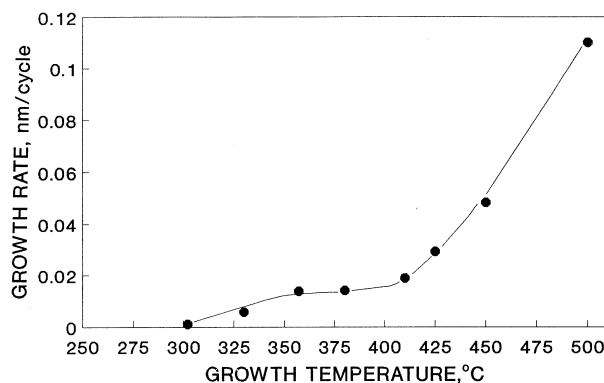

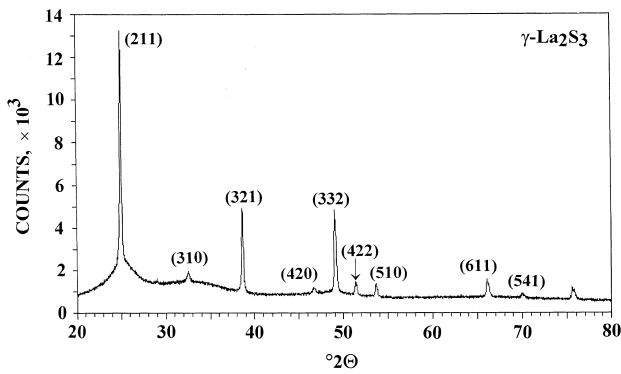Fig. 1. Dependence of film growth rate on growth temperature.

Fig. 2. Indexed X-ray diffraction pattern of γ-La$_2$S$_3$ thin film grown onto amorphous Al$_2$O$_3$/soda lime glass substrates at 500°C.
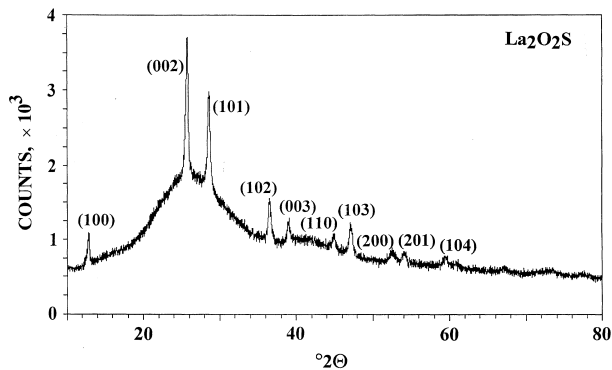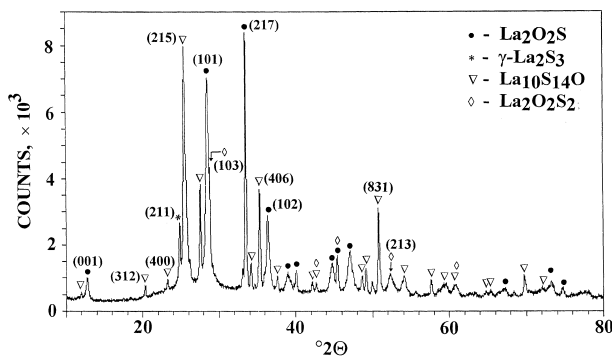

Fig. 3. Typical X-ray diffraction pattern of lanthanum sulfide film grown onto Corning 7059 glass substrates at 380°C and annealed for 1 h at 730°C.

the deposition temperature. Fig. 3 shows a typical XRD pattern of a film grown at 380°C and annealed at 730°C. The peaks in the XRD pattern can be assigned to hexagonal La$_2$O$_2$S [4]. The intensity of the peaks increased with annealing time. No other phases than La$_2$O$_2$S could be observed.

A different result was obtained when annealing the films grown at 500°C. The most pronounced peaks in the XRD pattern (Fig. 4) can be attributed to hexagonal La$_2$O$_2$S

[16] and to tetragonal La$_{10}$S$_{14}$O [4,16]. Only one well-defined peak at 24.8° still indicates the presence of γ-La$_2$S$_3$. Although the exact assignment of the relatively weak and broad peaks at higher 2θ values becomes ambiguous, few reflections could be taken as an evidence of co-existing La$_2$O$_2$S$_2$ [4] (Fig. 4).

3.2.2. X-ray photoelectron spectroscopy

According to the XPS measurements, no essential differences were observed in the films grown at 380 and 500°C. In addition, the composition of the films was almost independent on the location on the substrate surface. Amounts of lanthanum and sulfur were nearly equal at the surface, so the La$_2$S$_3$ thin film samples were not stoichiometric. In the bulk even more lanthanum than sulfur was detected. The same sulfur shortage has been observed earlier in ALE-grown SrS films [17]. As the samples were measured without any in situ cleaning in UHV, carbon, oxygen and, in some samples, fluorine contamination species were present at the surface. A depth profile of a crystalline La$_2$S$_3$ film grown at 500°C is presented in Fig. 5. Carbon was mainly present as adsorbed species at the film surface and the carbon content in the bulk was only 1–3 at.%. Fluorine concentration varied between 0 and 2.6 at.% at the surface. The F1s peak at 684.5±0.3 eV was defined as being due to LaF$_3$ [18]. The fluorine contamination probably originated from sample handling or from the lanthanum source material La(thd)$_3$. No sodium was detected in non-annealed samples, but some sodium appeared at the sample surface during annealing.

A significant feature of the thin films is the oxygen content which was, even in the bulk, about 20 at.% in non-annealed samples. Although the oxygen contents were similar in the films grown at 380 and 500°C, the former had lower La/O ratio. The oxygen 1s peak consisted of two components at the surface before and after annealing. The major component at binding energy 531.3±0.3 eV was defined as adsorbed and/or chemisorbed oxygen and the minor component at 528.6±0.3 eV was considered to be
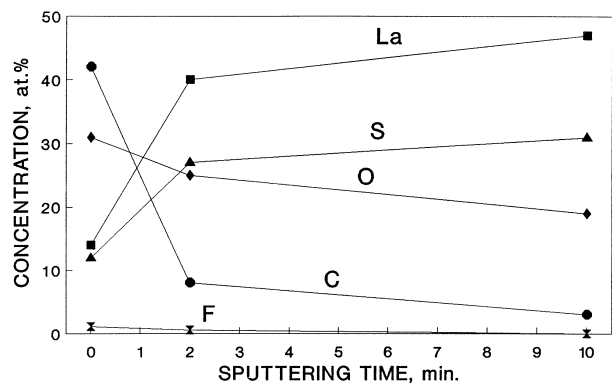

Fig. 4. Typical X-ray diffraction pattern of lanthanum sulfide film grown onto Corning 7059 glass substrates at 500°C and annealed for 1 h at 730°C.

Fig. 5. XPS depth profile of a crystalline La$_2$S$_3$ film grown at 500°C on soda lime glass substrate covered by Al$_2$O$_3$ ion barrier layer.

caused by La_2O_3 [13] or La_2O_2S which contains the $(LnO)_n^{n+}$ bonding system.

Sulfur was mainly present as a component of sulfide in as-deposited La_2S_3 samples. The location as well as the shape of sulfur 2p peak at 160.5 ± 0.3 eV was in good accordance with that in SrS thin films [17]. Pure or almost

Fig. 6. Lanthanum 3d XPS spectra of La_2S_3 film: (a) as-deposited, without any cleaning, (b) as-deposited, measured after sputtering, and (c) annealed, without any cleaning. La_2S_3 film was grown at 500°C on soda lime glass substrate covered by Al_2O_3 ion barrier layer.

pure sulfide was detected also in those films which were grown at 380°C and amorphous when checked by XRD. However, sulfur was partially oxidised during annealing, which was obvious from changes in the sulfur 2p spectrum. The new S 2p peak at 169 ± 0.3 eV was attributed to La_2O_2S [18]. The extent and rate of oxidation was dependent on the heating time and temperature.

The lanthanum 3d line shape showed that lanthanum was mainly present as lanthanum sulfide in both amorphous and crystalline samples before annealing. Besides measuring the La 3d spectra of as-deposited crystalline films (Fig. 6a), the spectra were also recorded after sputtering (Fig. 6b) and annealing (Fig. 6c). The spectrum in Fig. 6b is in good accordance with that reported for La_2S_3 [19]. Some small changes in the lanthanum 3d spectra were detected after annealing the films (Fig. 6c). The changes were more obvious, the more sulfide was oxidised. Lanthanum sulfide was oxidised to lanthanum oxysulfide during heat-treatment and the oxygen residues detected in the films were probably responsible for the post-annealing formation of the oxysulfide crystallites detected also by X-ray diffraction (Fig. 3).
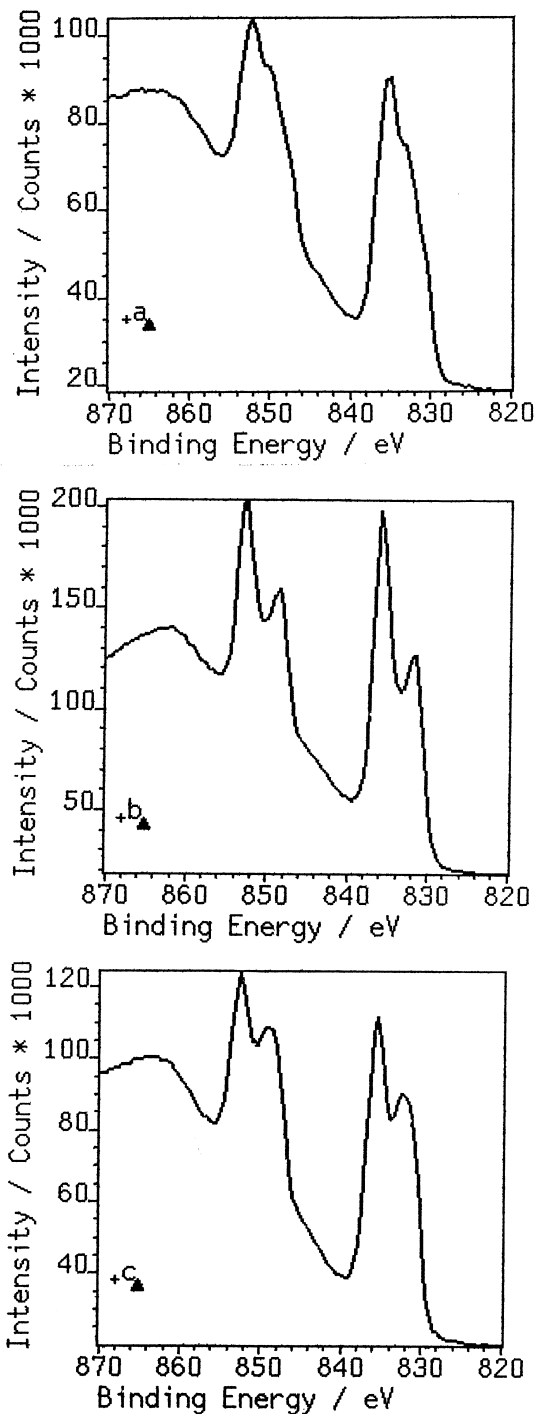
4. Conclusion

By combining optical, XRD and XPS data, it has been shown for the first time that thin films of γ-La_2S_3 can be grown at a relatively low temperature of 500°C or even below this. The films contain, however, a significant amount of oxygen and carbon, probably originating from the β-diketonate ligand. Carbon may originally stabilize the γ-La_2S_3 [15], while the effect of oxygen is apparent in annealing. Although annealing was carried out in an inert environment, the residual oxygen in the bulk of the film is more than sufficient to form oxygen-containing species, especially La_2O_2S which is stable over a wide temperature range [3,20] compared to the high-temperature γ-La_2S_3, which is usually prepared only at temperatures well above 1000°C. When the La/O ratio is higher and the films are grown at 500°C, the annealing results in a mixture of phases (Fig. 4), but when there is originally enough oxygen (lower La/O ratio) and the structure is amorphous, La_2O_2S is the only crystalline phase detected after annealing (Fig. 3).

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