Journal of Alloys and Compounds 275–277 (1998) 742–745

Rare earth-doped alumina thin films deposited by liquid source CVD processes

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Abstract

Two types of liquid-source CVD processes are proposed for the growth of rare earth-doped alumina thin films suitable as amplifying media for integrated optic applications. Amorphous, transparent, pure and erbium- or neodymium-doped alumina films were deposited between 573 and 833 K by atmospheric pressure aerosol CVD. The rare earth doping concentration increases by decreasing the deposition temperature. The refractive index of the alumina films increases as a function of the deposition temperature from 1.53 at 573 K to 1.61 at 813 K. Neodymium-doped films were also obtained at low pressure by liquid source injection CVD. © 1998 Elsevier Science S.A.

Keywords: Thin films; CVD; Rare earth; Alumina; Integrated optics

1. Introduction

The development of optical telecommunication components requires the realization of active optical materials, especially as thin films, in order to integrate both optical and electronic functions on the same chip. In contrary to the fiber applications, for integrated devices, where a high efficiency of optical amplification is required, the classical rare earth-doped silicate glasses are strongly limited by the cooperative upconversion effects which occurs at high rare earth concentration in this material due to the rare earth clustering [1]. In order to avoid this phenomenon, recently crystalline host materials such as alumina have been proposed as amplifying media [2,3]. Moreover, these kinds of materials theoretically exhibit a low level of phonon losses. As a first step in the realization of a complete amplifying structure, this paper reports the growth of erbium- or neodymium-doped alumina films by two different liquid source CVD processes.

2. Experimental

The first process works at atmospheric pressure and the solution is introduced in the reaction chamber as an aerosol [4]. This aerosol is obtained by an ultrasonic spraying system which guarantees a narrow dispersion of the droplets size. This process could be also summarized by the acronym APACVD (atmospheric pressure aerosol CVD) and it has been developed in our laboratory for the deposition of oxide films for magnetic applications [4] and gas sensor applications [5]. The second process works at low pressure (5 hPa) with a cold wall configuration. The main characteristic of this reactor is that the solution is introduced by an droplet injector similar to the one used in cars for the electronic injection of the petrol. This process can be called liquid source injection CVD (LSICVD) and has been first developed for dielectric films [6]. For the two processes the source solution is obtained by dissolving, in an organic solvent, organometallic precursors, similar to these used for MOCVD. Table 1 Table 2 present the experimental conditions used for each process. The refractive index and the thickness of the films were measured by ellipsometry with a Gaertner L116B apparatus at 632.8 nm.

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PII: S0925-8388(98)00433-2

Table 1
Atmospheric pressure aerosol CVD - deposition conditions

Precursors: $Al(AcAc)_3$ [$Al(C_5H_7O_2)_3$], $Er(AcAc)_3$ or $Nd(C_{11}H_{19}O_2)_3$
Solvent: butanol
Concentration: 0.02 mol l^{-1}
Pressure: atmospheric

Ultrasonic frequency: 800 kHz
Aerosol flow: 2 cc min^{-1}
Carrier gas flow, 4 l min^{-1} (air)
Temperature: 573–833 K
Substrate: 100 silicon wafers or silica

Table 2
Liquid source injection CVD: deposition conditions

Precursors: $Al(OC_4H_9)_3$, $Nd(C_{11}H_{19}O_2)_3$
Solvent: monoglyme ($C_4H_{10}O_2$)
Concentration: 0.2 mol l^{-1}
Pressure: 5 hPa

Injection frequency: 1 Hz
Injection open time: 2 ms
Temperature: 723–923 K
Substrate: 100 Silicon wafers

3. Results

3.1. Atmospheric pressure aerosol CVD

As liquid source solution, aluminium acetylacetonate ($Al(AcAc)_3$) is dissolved in butanol at a concentration of 0.02 mol l^{-1}. Deposition conditions are summarized in Table 1. The dependence of the alumina film growth rate vs. the deposition temperature is reported on Fig. 1. The growth starts at a relatively low temperature (200 nm h^{-1} at 553 K). Then at low temperatures the growth is surface reaction limited until 673 K. At higher temperature the diffusion-limited behavior is not well observed because it is quickly screened by the depletion of the partial pressure of the precursor vapor, which induces a decrease of the growth rate. The doped films exhibit the same behavior. Moreover, the growth rates increase with increasing precursor concentration, which means that the saturation conditions of the vapor phase are not reached.

In order to perform the rare earth (R) doping, a small amount of erbium acetylacetonate ($Er(AcAc)_3$) or neodymium tetramethylheptanedionate ($Nd(TMHD)_3$ or $Nd(C_{11}H_{19}O_2)_3$) are dissolved in the source solution. The compositions of the doped films were measured by electron probe microanalysis (EPMA) and computed by help of a special software dedicated to the thin film analysis

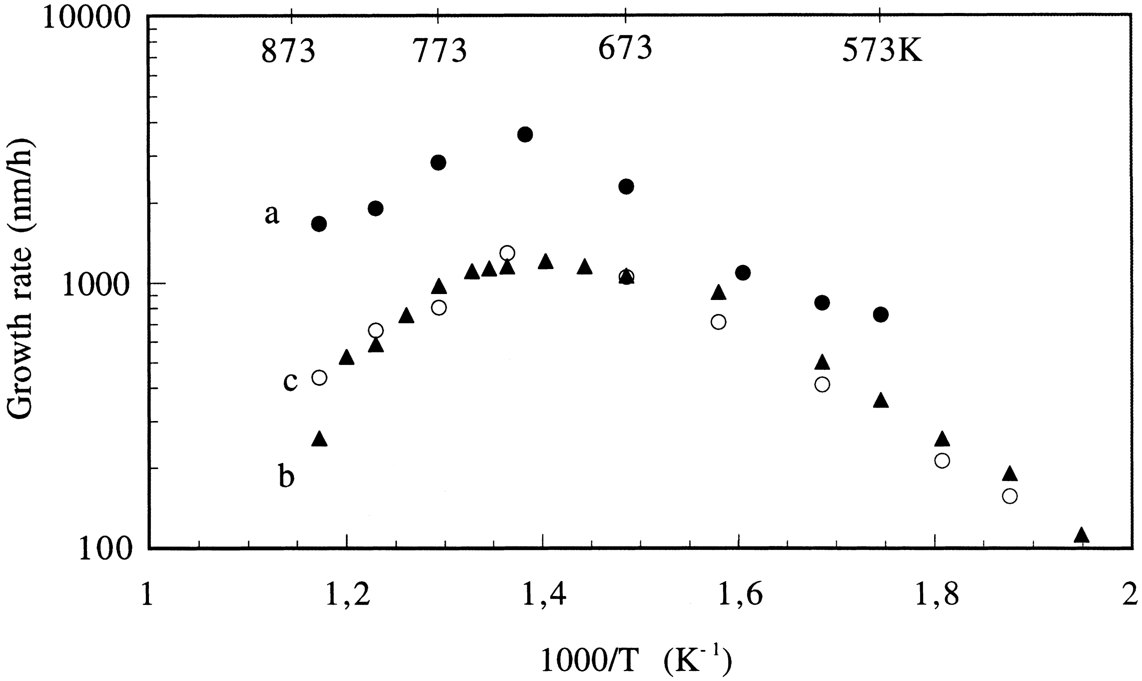

Fig. 1. Arrhenius plot of the film growth rate versus the deposition temperature for: (a,b) pure alumina films deposited with a precursor concentration of 0.05 and 0.02 mol l^{-1}, respectively; (c) erbium-doped alumina films deposited with a solution concentration of $Al(AcAc)_3$–0.02 mol l^{-1} and $Er(AcAc)_3$–0.002 mol l^{-1}.

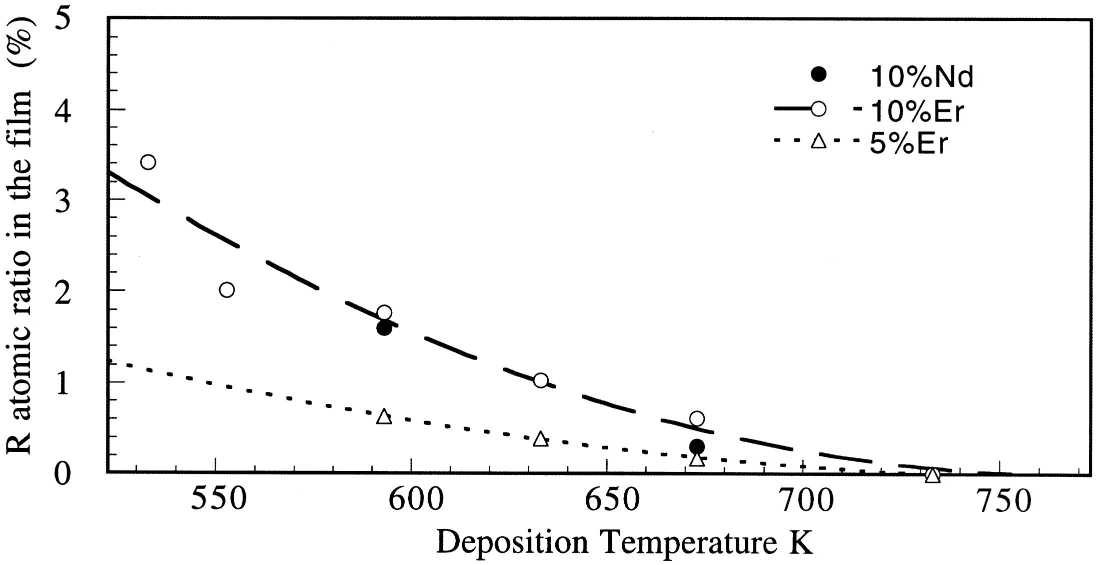

Fig. 2. Rare earth concentration in the film (R atomic ratio, %) versus the deposition temperature for different R/Al atomic ratio in the solution.

('strata' software) [7]. The results are plotted on Fig. 2. For the same composition of the solution (atomic ratio Er/Al 5 or 10%), the concentration of erbium in the film (atomic ratio Er/(Al+O+Er) %) increases by decreasing the deposition temperature. Above 733 K the erbium doping is not detectable. This result is consistent with the fact that the deposition of pure erbium oxide occurs only between 573 and 753 K under the same experimental conditions. However, for pure erbia films, the addition of 5% by volume of acetylacetone to the solution increases the deposition temperature range and allows to carry out the deposit, between 813 and 873 K. For the neodymium a similar increase for the doping concentration is observed when the deposition temperature decreases.

As observed with a skew view of a film crosssection by scanning electron microscopy (SEM), the deposited films appear to be very smooth (Fig. 3). For all the deposition temperatures, X-ray diffraction pattern observations reveal that doped and non-doped films are amorphous (Fig. 4). Such a state does not change after annealing at 1073 K for 1 h. Only the series of the erbia films, deposited above 813 K with the addition of acetylacetone to the solution, exhibit a polycrystalline structure.

The films deposited onto silicon were characterized by ellipsometry. The refractive index of the alumina films increases as a function of the deposition temperature from 1.53 at 573 K to 1.61 at 813 K (Fig. 5). This increase is connected with the density increase from 1.5 to 2.8 in the same temperature range (Fig. 5). The density was determined from the film thickness measured by ellipsometry and the data of EPMA, using the 'strata' software. The films deposited onto silica exhibit a high transparency, and the first M-lines experiments show that a 1.7-μm thick pure alumina film deposited onto silica at 633 K forms a monomode planar waveguide at 1.55 μm.

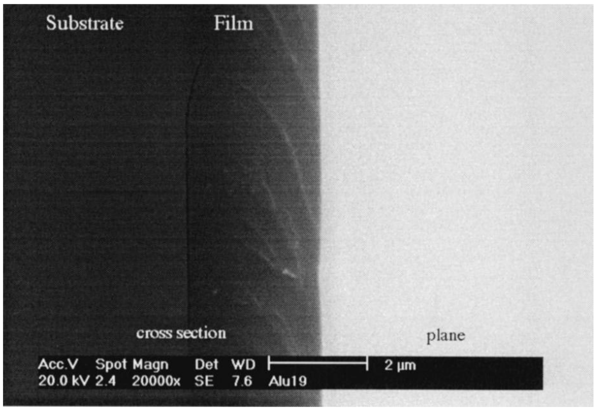

Fig. 3. SEM micrograph of a skew view of the crosssection of a typical alumina film deposited at 633 K.

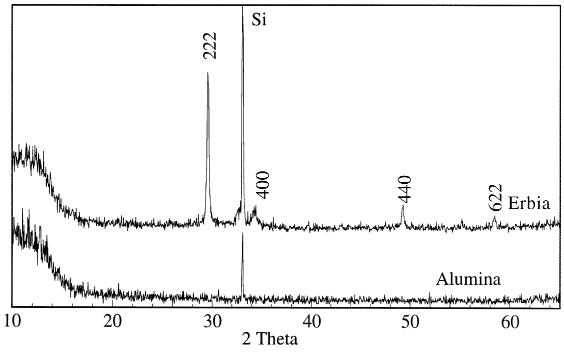

Fig. 4. X-ray diffractogram of an erbium-doped alumina film and a pure erbia film deposited at 633 and 813 K, respectively.

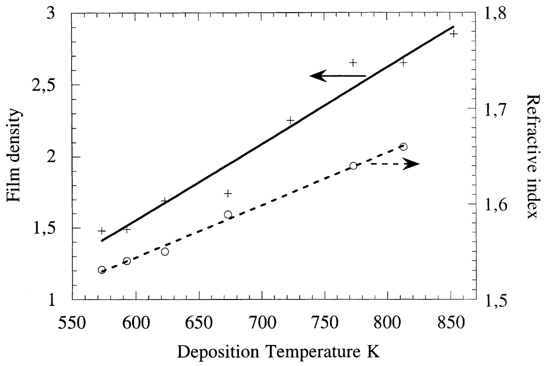

Fig. 5. Density and refractive index of alumina thin films versus the deposition temperature.

3.2. Liquid source injection CVD

In this case, the precursors are aluminium *s*-butoxide and neodymium TMHD. The solvent used is the monoglyme (1,2-dimethoxyethane) and the total precursor concentrations is 0.2 mol l^{-1}. Amorphous alumina thin films were also obtained in the temperature range of 723–923 K. The deposition rate reaches 2 μm h^{-1} and the thin films exhibit a very smooth surface. From a solution such as neodymium/aluminium with an atomic ratio equal to 10%, doped films with a neodymium atomic concentration of 0.1–0.2% were obtained at 823 and 873 K, respectively. The refractive indexes are 1.63 and 1.66, respectively, for a thickness of about 0.6 μm. In this case the density of the films varies from 2.8 to 3.0.

4. Conclusion

By using two types of liquid source CVD processes we have succeeded in depositing erbium- or neodymium-doped alumina thin films. With the atmospheric pressure aerosol CVD process the rare earth-doped films were obtained between 573 and 733 K; whereas with the low-pressure liquid injection CVD they were obtained at higher temperature (823–873 K). The films were transparent, amorphous and smooth. The knowledge of the growth conditions will allow the investigation of the optical attenuation and the rare earth spectroscopic properties.

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