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SYNTHESIS OF SAMARIUM OXIDE FILMS BY PULSED LASER DEPOSITION

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ABSTRACT

Uniform Samarium oxide (Sm_2O_3) films were grown on 75-mm diameter silicon wafers by the pulsed laser deposition (PLD) technique. The beam of a KrF excimer laser was used to ablate an Sm_2O_3 target in an oxygen pressure of 30 mTorr. The crystal structure, surface morphology and optical properties of films deposited at a temperature range of 25~680°C were determined by XRD, FE-SEM, and spectra reflectance. Monoclinic structure was the predominant phase for Sm_2O_3 films deposited at temperatures of 400°C and 680°C. Amorphous or partially crystallized amorphous phase was observed at deposition temperatures of 25°C and 200°C. The Sm_2O_3 film deposited at 680°C is very dense, while films deposited at lower temperatures have higher porosity. The values of index of refraction, n, and extinction coefficient, k, at λ = 633 nm are 1.867 and 0.0660, respectively, for the film deposited at 680°C, and are in a range of 1.5~1.6 and 0.01~0.04 respectively for films deposited at lower temperatures.

INTRODUCTION

The Si-based technology is expected to continuously shrink the device size [1], therefore, there is an urgent need to look for new dielectrics to replace amorphous SiO_2 in applications such as gate dielectrics in metal-oxide-semiconductor field effect transistors (MOSFETs) and in capacitors for dynamic random access memory (DRAM) storage cells. Any scaling down the Si-based MOSFETs will result in a reduced thickness requirement for the SiO_2 dielectric layer to below 2 ~ 3 nm. With such a small thickness, the direct tunneling of electrons will occur that lead to large leakage current. The new gate dielectric, whose permittivity, ε, is substantially greater than SiO_2 (ε ~ 3.9), the thickness of the dielectric layer could be larger in the ratio $\varepsilon/\varepsilon_{SiO2}$ and have the same electrical effect, can avoid the large leakage current. For Si-based DRAM, the continuously scaling down of the size of individual capacitor will also require the use of new dielectrics with high permittivity in order to keep the same capacitance value. However, when considering a new dielectric to replace SiO_2, various other criteria, including Si/metal-dielectric barrier height, dielectric-Si reactivity [2], and leakage current, must be met [3].

The rare-earth oxides (RE_2O_3) might be considered as candidates [4] for the replacement of SiO_2 in gate dielectric/memory cell applications in the intermediate timescale. Epitaxial films of Gd_2O_3 and Y_2O_3 have been obtained [5] with dielectric constants of 14 and 18 respectively. Similar values (13.6 and 16) were obtained for ostensibly amorphous films deposited by electron beam evaporation followed by low temperature re-oxidation [6].

Another rare-earth oxide, Samarium oxide, is also attractive for replacing SiO_2 in microelectronic and opto-electronic device applications due to its high dielectric constant and low likelihood of interaction with silicon substrate during processing to form silicates. However,

there is very limited information available on the Samarium oxide thin film. In the present work, Sm_2O_3 thin films were deposited by the laser ablation of an Sm_2O_3 target in the presence of oxygen. To our knowledge, this is the first report on the PLD of this material. The results of crystal structure, morphology and optical properties of those Sm_2O_3 films are presented.

EXPERIMENTAL

A schematic diagram of our large-area PLD system in Integrated Manufacturing Technologies Institute (IMTI) is shown in Figure 1. Detailed information about our PLD system

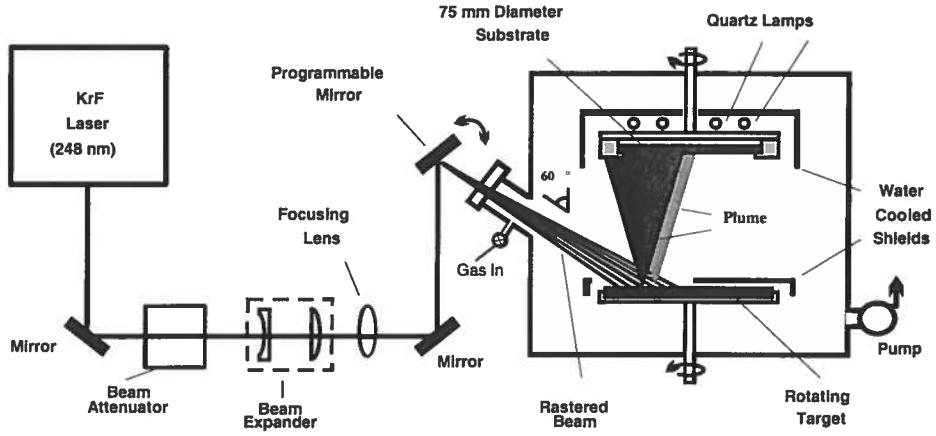

Figure 1: Schematic of the PLD set-up

has been described previously [7]. The Sm_2O_3 films were deposited by ablating a 90 mm diameter rotating Sm_2O_3 target (Sm_2O_3, stoichiometric, 99.9%, Super Conductor Materials Inc.) in an advanced deposition chamber (PVD. Inc., PLD-3000) by means of a pulsed KrF excimer laser (λ = 248 nm, Lambda Physik, LPX-210i), at a repetition rate of 50 Hz. A 75 mm diameter silicon wafer (p-type Si<100>, ρ = 10-30 Ω. cm) was used as a substrate for the PLD of Sm_2O_3 films. To achieve uniform deposition over the entire substrate surface, the laser beam was rastered over the radius of the rotating target. A programmable kinematic mount was used to control the rastering movement of the last mirror in the optical train.

Before introducing a wafer into the deposition chamber, it was cleaned by HF according to the procedure that was described previously [7]. After loading, the process chamber was pumped down below 2×10^{-6} Torr using a turbo-molecular pump. A blackbody-type heater that used quartz lamps on the top of the wafer, allowed non-contact, radiation-based heating. When the temperature reached the preset value, oxygen gas (99.995%, Air Liquid) was introduced into the chamber and its flow was controlled through a mass-flow controller to achieve an oxygen gas pressure of 30 mTorr. The laser was then turned on and a pre-cleaning cycle of the target was performed for two minutes. Subsequently, the shutter that hid the substrate surface from the ablation plume was opened and the deposition started. After a given processing time, the laser was stopped and the substrate was allowed to cool down. The on-target laser beam fluence was adjusted to about 2 ~ 3 J/cm^2.

The structure of the Sm_2O_3 films was examined by X-ray diffraction (XRD, Philips, X-Pert MRD) in the θ_0-2θ thin film configuration, where θ_0 was fixed at a value of 1°. The thickness, refractive index and extinction coefficient were simultaneously evaluated in the 250-850 nm

ranges using a fiber-optic-based spectrophotometer (Scientific Computing International, Film Tek 3000). A generalized Lorentz oscillator model, developed by SCI, was used for curve fitting. A Hitachi's FE-SEM S-4800 using the new super ExB filter technology was used to examine the morphology of Samarium oxide films. FE-SEM graphs were taken at a magnification of 250,000.

RESULTS AND DISCUSSIONS

Uniform Sm_2O_3 films were successfully grown on the 75-mm diameter Si wafer. For the film deposited at a substrate temperature of 200°C, the uniformity of film thickness, and optical properties across the 75-mm diameter wafer was shown in Figure 2. The normalized thickness of the Sm_2O_3 films was measured by a spectral reflectance technique along the radial position across the wafer and presented in Figure 2a. The PLD Sm_2O_3 thin film is uniform with an average thickness of 117.6 nm and the average deviation across the wafer below 2.0 %. The dependence of the refractive index, n, on the radial position across the wafer is also presented in Figure 2b, for the same film. The index, n, is given for λ = 633 nm and its average values is n = 1.60. The average deviation of n across the wafer is also below 2.0 %. Similar uniformity of thickness and optical properties were obtained for Samarium oxide films deposited at other temperatures.

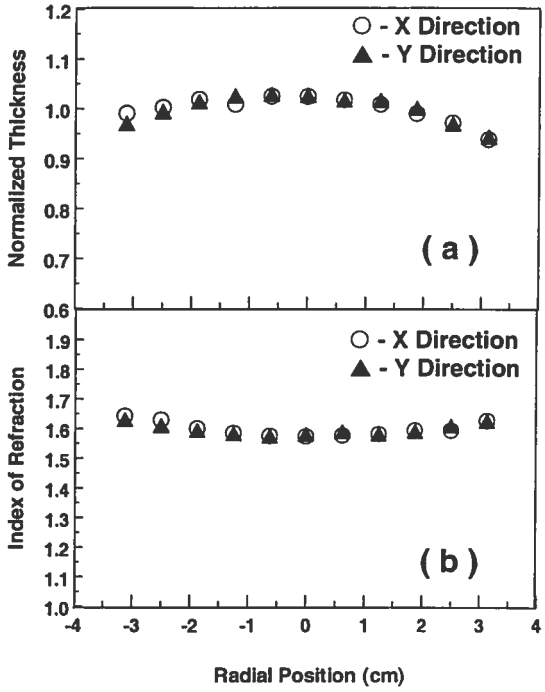

Figure 2: Normalized thickness (a) and index of refraction (b) of the Sm_2O_3 film deposited at 200 °C as a function of the radial position.

Figure 3 presents the XRD spectra of Sm_2O_3 films deposited at substrate temperatures of 25, 200, 400 and 680°C. XRD pattern of Sm_2O_3 target that used to grow Sm_2O_3 films is also shown in the figure for comparison. The XRD spectrum of the Sm_2O_3 target was obtained by X-ray diffraction in the θ_0-2θ configuration, where θ_0 varies. Its XRD pattern can be assigned to monoclinic Sm_2O_3 structure (ICDD 43-1030). Figure 3 shows that, in general, the XRD pattern of the Sm_2O_3 film becomes more well-defined with an increase in the substrate temperature. The diffraction pattern of the 25°C

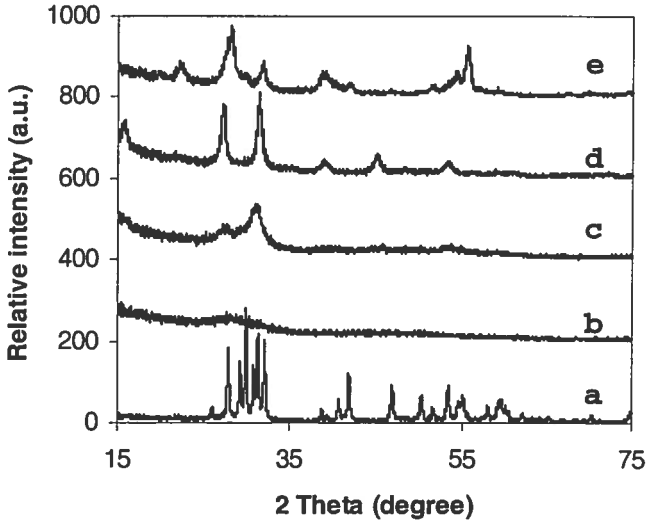

Figure 3: XRD spectra of Samarium oxide target (a) and Samarium oxide films deposited at 25°C (b), 200 °C (c), 400°C (d) and 680 °C (e).

Sm_2O_3 film (Figure 3 curve b) consists of a diffuse-scattering curve with a broad band centered at 2θ of about 28°. Such a profile indicates an amorphous-like structure for the film. For Sm_2O_3 films deposited at 200, 400 and 680°C (Figure 3 curves c, d and e), all the XRD peaks were broad and not well defined, which makes the assignment of those peaks very difficult. There are two possible reasons that cause the broadening of those XRD peaks. One is the low crystallinity of films at those deposition temperatures, and the other is the small grain size of films grown by PLD. For a low symmetry monoclinic Sm_2O_3 structure, many diffraction peaks were located at angles that are very close to each others. When the crystallinity is low and the grain size is small, those diffraction peaks merge and become not well resolved. Figure 3 shows that the crystallinity of Sm_2O_3 films increased with increasing the temperature. The 200°C data can be regarded as a partially crystallized amorphous phase, while the XRD pattern of the film deposited at 400°C was more difficult to identify. Two diffraction peaks, measured at angles of $2\theta = 15°$ and 45°, cannot be attributed to any of the current structures listed in the ICDD database for known oxides of Samarium. These peaks may be ascribed to a crystalline silicate layer, such as Sm_2SiO_5 (ICCD 40-0285), and/or Sm_2SiO_4 (ICDD 20-1023). Those Samarium silicates may become unstable at higher substrate temperatures. However, we can be certain that the film deposited at 400°C also contains a predominant monoclinic phase. The crystal structure of the film deposited at 680°C determined from its XRD pattern can be more ascertained to a polycrystalline with monoclinic symmetry.

In the spectral reflectance characterization of Sm_2O_3 films, excellent fitting on the reflectance curves was obtained by assuming a single film on top of the silicon substrate. The interface transition region was believed to be too thin with respect to the Sm_2O_3 coatings (> 100 nm) to affect the measurements. A generalized Lorentz model developed by Scientific Computing International (SCI) was used for curve fitting with two oscillators being used. The refractive index, n, and extinction coefficient, k, of the films deposited at both 400°C and 680°C determined at the wavelength range of 250 to 850 nm are presented in Figure 4. Values of n at both temperatures decrease with increasing the wavelength, while values of k increase with an increase in the wavelength. The n and k at $\lambda = 633$ nm for films deposited at 25, 200, 400 and 680°C are presented in Table 1. The n and k data are average values determined for three samples at each

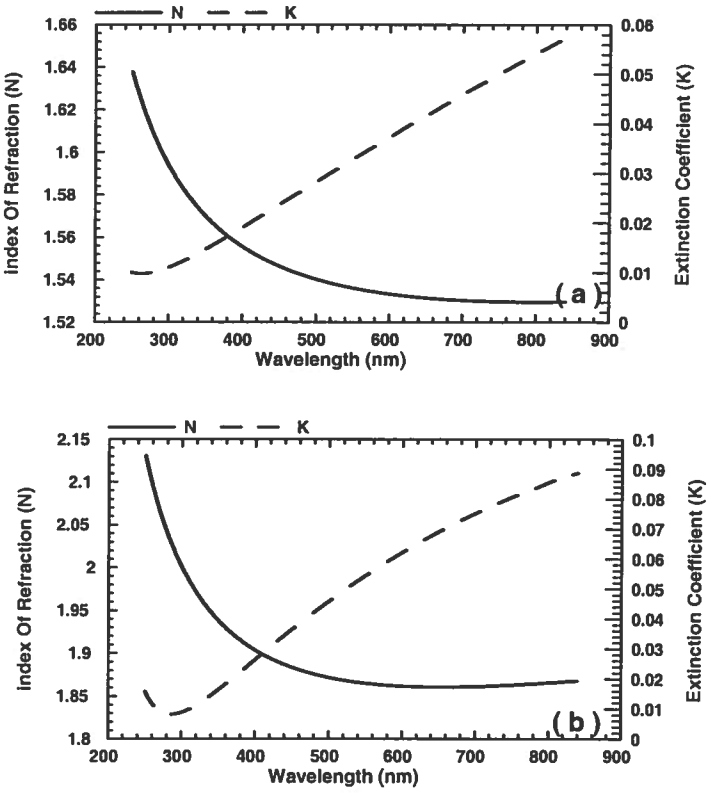

Figure 4 : Dispersion curves of the index of refraction, n, and extinction coefficient, k, of a Samarium oxide films deposited at: (a) 400°C, and (b) 680°C.

deposition temperature. The refractive index of 1.867 observed for the film deposited at 680°C is close to the published value [8] for monoclinic Sm_2O_3 of 2.095 (λ = 589.3 nm). The Lorentz-Lorenz formula [9] relates the density of the film(ρ), and the refractive index(n):

$$(n^2 - 1)/(n^2 + 2) = (4\pi/3)\,\alpha_{opt}\,\rho/M \qquad (1)$$

where α_{opt} is the infinite frequency molar polarizability and M the molar mass. Using the measured values of n for all the films and assuming, to first order, that α_{opt} does not vary with density we can crudely estimate the relative density of films deposited at various temperatures. The results are shown in Table 1. The film deposited at 680°C has the highest density, while the densities for films deposited at other three temperatures are similar and are only about 70 ~ 80% of the density of the film deposited at 680°C. Density reduction could result from porosity and/or incorporation of terminating carbon related groups into the film. The corresponding very low extinction coefficients for all films are indicative of low absorbing deposits at the investigated wavelength region.

Table 1: The refractive index(n), extinction coefficient(k), and density(ρ), of Sm_2O_3 films deposited at 25°C, 200°C, 400°C, and 680°C.

Sm_2O_3 Film / Deposition Temperatures	n	k	Relative density (ρ_T/ρ_{680})
25°C	1.610	0.0012	0.800
200°C	1.588	0.0042	0.780
400°C	1.534	0.0396	0.728
680°C	1.867	0.0660	1.000

Figure 5 shows the FE-SEM micrographs of Samarium oxide films deposited at a temperature of 25 (a), 400 (b) and 680°C (c). 25°C film contains columnar-like structure with a size of about 20 nm oriented perpendicularly to the substrate and has very high porosity. The film deposited at 400°C contains triangle-shaped gains oriented randomly to the substrate and it is also very porous. The film deposited at 680°C is very dense and contains large triangle-shaped and small irregular-shaped gains. The FE-SEM results are consisted with the previously described XRD and spectra reflectance results.

The electrical properties of the PLD Sm_2O_3 films deposited at 400°C and 680°C have also been examined. The detailed results will be reported elsewhere. The dielectric constant of the film deposited at 400°C is found to be ~ 9.6 whilst for the film deposited at 680°C it is 12.8. Although the dielectric constants are satisfactory for its use as a new dielectric

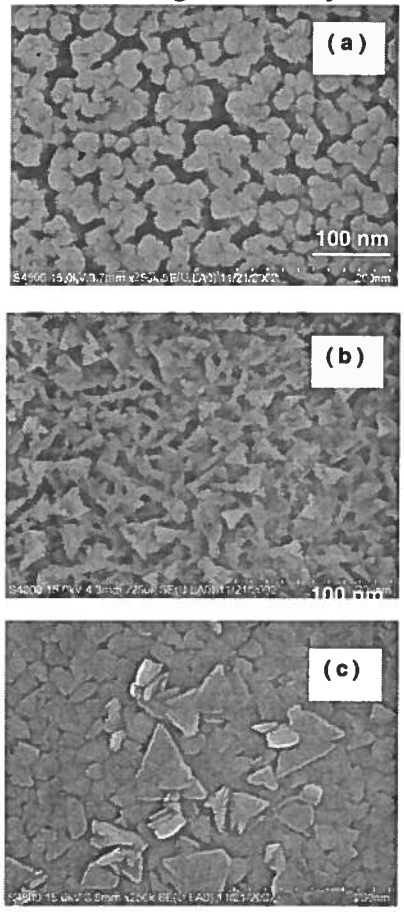

Figure 5: FE-SEM graphs of Sm_2O_3 films deposited at a substrate temperature of (a) 25, (b) 400, and (c) 680°C.

material, the magnitude of the leakage current for reasonable electric fields is prohibitive for application of these films as gate dielectrics for MOSFETs. Further work is required to ascertain the origin of the leakage current to try to reduce it to technologically acceptable levels.

CONCLUSIONS

Samarium oxide films were deposited on silicon substrates by PLD, at oxygen pressures of 30 mTorr and a temperature of 25, 200, 400, and 680°C. XRD analysis reveals that the crystal structure of Sm_2O_3 film deposited at 25°C is essentially amorphous, while the film deposited at 200°C is a partially crystallized amorphous. The film deposited at 680°C is ascertained to be a polycrystalline with monoclinic symmetry. The 400°C films can be described as a predominant monoclinic phase. Dense film was obtained at a deposition temperature of 680°C, while very porous films were obtained at deposition temperatures of 25, 200 and 400°C. The values of n and k at λ = 633 nm are 1.867 and 0.0660 for the film deposited at 680°C, and are in a range of 1.5~1.6 and 0.04~0.01 respectively for the film deposited at lower temperatures.

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