Effects of rapid thermal process on structural and electrical characteristics of Y$_2$O$_3$ thin films by r.f.-magnetron sputtering

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Abstract

Y$_2$O$_3$ thin films have been deposited on (100) Si substrates by r.f.-magnetron sputtering and subsequently submitted to rapid thermal processing (RTP). X-ray examinations show that the sputtered Y$_2$O$_3$ was dominated by the (111) cubic structure. With increasing RTP temperature (> 700 °C), the crystallinity of films was improved, especially for the intensity of (400) diffraction peak. The as-deposited films show good dielectric properties in terms of a relative dielectric constant of 16.67 and leakage current density of 6 × 10$^{-7}$ A cm$^{-2}$ (at 1.8 MV cm$^{-1}$). After the RTP treatment, both the dielectric constant and leakage current of Y$_2$O$_3$ were found to decrease. A typical dielectric constant decreased to 14.77 and its leakage current density lowered to 3 × 10$^{-8}$ A cm$^{-2}$ (at 1.8 MV cm$^{-1}$) for the film annealed at 850 °C. The observed behavior of dielectric constant may be due to the intermediate oxide formation between Y$_2$O$_3$ and Si. Capacitance-voltage characteristics confirm that the reduction of leakage current at high electric field comes from the improvement of interface states.

Keywords: Dielectric properties; Metal-oxide semiconductor structure; Sputtering; Yttrium oxide

1. Introduction

Thin films of high dielectric permittivity and breakdown strength have a potential application in electroluminescent (EL) devices [1-3]. These films in the EL structure can provide the current limiting necessary to prevent device failure. Specifically, they must have a charge storage capacity at breakdown that is at least three times that of the phosphor layer [4]. Among the materials investigated, Y$_2$O$_3$ has been regarded as one of the more promising candidates for the dielectric insulator of EL devices [5-7]. Several deposition methods, including r.f. sputtering, electron-beam, and thermal evaporation techniques [8-10] were attempted to study the structural, electrical or mechanical properties of Y$_2$O$_3$ films. It has been concluded that the sputtered Y$_2$O$_3$ thin film is superior to the other deposited ones because the former has excellent stoichiometry control [11]. In order to further improve the sputtered material properties, post-growth thermal annealing is usually employed. The annealing effects on the properties of the Y$_2$O$_3$ insulator have not been investigated extensively. Moreover, the non-stoichiometry problem would be an important issue for the thermally annealed EL devices, especially using the traditional furnace process. Such a process is also not desirable for the monolithic integration of EL and Si-based devices, since junction softening may occur for the components of the drive circuitry. Thus, decreasing the annealing time and increasing the process temperature are expected to benefit the post-treatment results. In this work, Y$_2$O$_3$ thin films were deposited by r.f.-magnetron sputtering, and then subjected to a rapid thermal processing (RTP). The effects of RTP on the material characteristics of Y$_2$O$_3$ films will be described.

2. Experimental

Thin films of Y$_2$O$_3$ were deposited on p$^+$-type (100) Si substrates ($\sim$ 0.005 Ω cm) by r.f.-magnetron sputtering. All the depositions were performed in an in-situ tilted multi-electrode system as shown in Fig. 1. The growth chamber consists of three magnetron electrodes oriented so that all cathodes are equidistant from the substrate ($\sim$ 10 cm). This system is used primarily for the fabrication of double-insulator EL structures, facilitating the growth of each layer without breaking vacuum to change targets. A base pressure of $\sim$ 2 × 10$^{-7}$ Torr can be pumped down by the use of a vacuum load-lock chamber and liquid-nitrogen baffle.

The source material for this study was a 1.5 inch diameter Y$_2$O$_3$ target with 99.99% purity, and the films were deposited using only argon as the sputtering gas. During the deposition,
the substrate was heated at a constant temperature (100–300 °C), and rotated to insure uniform film growth over the exposed region. The Y$_2$O$_3$ films of thickness 200–300 nm were deposited at a sputtering pressure of $7 \times 10^{-4}$ Torr with 4.4 W cm$^{-2}$ applied to the target. Post-thermal treatment (700–850 °C) for the as-deposited Y$_2$O$_3$ samples was carried out with a Jetfirst processor (Jipelec Corp., France). The heating rate used was about 100 °C s$^{-1}$, and soaking time was 60 s. The process temperature was monitored by a small K-type thermocouple contacting the backside of the sample wafer. Oxygen was flowed into the RTP chamber to maintain the stoichiometry of the dielectric film, and the samples were then cooled with the chamber door opened. For comparative studies of the RTP effect, samples obtained from a single Y$_2$O$_3$ deposition run were used.

Crystallinity of the Y$_2$O$_3$ samples was investigated by X-ray diffraction with Cu Kα radiation. Electron probe microanalysis (EPMA, JEOL JXA-8800) was used to determine the stoichiometry of the deposited films. A dry etching process was adopted to define a step in the film down to the Si surface, and the height was then measured using a Dektak 3030 profilometer. The bonding structures of the films were also characterized by a Bio-Rad Fourier transform infrared (FTIR) spectrometer (FTS-40). All dielectric and electrical characteristics were measured in the metal–insulator–semiconductor (MIS) configuration with aluminum as the top and bottom electrodes. The top contact (300 nm) was thermally evaporated through a metal mask to produce circular diodes of 0.3 mm diameter. A back ohmic contact to the p$^+$-Si wafer was made by the deposition of a 500 nm thick Al film. Current–voltage ($I$–$V$) and capacitance–voltage ($C$–$V$) measurements were performed in a darkened probed station using the HP 4145B semiconductor parameter analyzer and HP 4194A impedance analyzer, respectively. The obtained data was taken from the average value of five measured diodes distributed over each sample.

3. Results and discussion

From EPMA examinations, the stoichiometry of the Y$_2$O$_3$ samples is determined as 1.49, and has no evident variation with the deposition temperatures used in our experimental range. The value of refractive index measured by a He–Ne laser is $\sim 1.91$ which agrees well with the value reported for bulk Y$_2$O$_3$ [12]. Fig. 2 shows the X-ray diffraction patterns of the Y$_2$O$_3$ films subjected to different RTP temperatures, as compared with that of the as-deposited sample. It was found that the sputtered-Y$_2$O$_3$ thin films strongly oriented their (111) axis of cubic structure. Once the samples were thermally annealed, the crystal quality of the films was improved and the intensity of (400) diffraction peak showed a substantial enhancement with increasing the RTP temperature. The present result suggests that Y$_2$O$_3$ films could recrystallize to some extent based on the (100) Si substrate during the annealing process.

For a typical EL device structure, a figure of merit for the insulator is the charge storage capacity ($\varepsilon_0\varepsilon_rE_{dc}$), where $\varepsilon$ is...
the relative dielectric constant, \(\varepsilon_r\) the permittivity of vacuum, and \(E_{bd}\) the breakdown strength. As concerning the \(\varepsilon_r\) and \(E_{bd}\) behaviors of the RTP-treated \(\text{Y}_2\text{O}_3\) films, they will be discussed as follows. The MIS diodes for the samples with and without RTP can be swept from depletion to accumulation by applying positive to negative d.c. bias to the top Al electrode. The dielectric constant of the \(\text{Y}_2\text{O}_3\) can therefore be determined from the measured value of accumulation capacitance (\(C_{acc}\)), using the relation:

\[
C_{acc} = \varepsilon_r \varepsilon_0 A/d
\]

where \(A\) is the area of diode, and \(d\) the thickness of dielectric layer. Fig. 3 displays the obtained \(\varepsilon_r\) value as a function of the RTP temperature. The arrow shown in this figure is the corresponding \(\varepsilon_r\) value (16.67) for the as-deposited \(\text{Y}_2\text{O}_3\) films. It is found that the \(\varepsilon_r\) value shows a slight decrease to 14.77 as the RTP temperature increases to 850 °C. The result is contrary to the theoretical expectation where the higher crystalline property of the dielectric film yields a larger \(\varepsilon_r\) value. The discrepancy may be due to the fact that \(\text{Y}_2\text{O}_3\) film is very transparent to oxygen diffusion. Consequently, oxygen coming from the annealing ambient could enable growth of the intermediate thin oxide between \(\text{Y}_2\text{O}_3\) and Si. The observed FTIR spectra for the above samples can further support this point. The FTIR peak at about 1080 cm\(^{-1}\) due to the Si-O asymmetric stretching mode is found to enhance in its integral intensity as the RTP temperature increases. Similar results have also been described by Rastogi and Sharma in their \(\text{Y}_2\text{O}_3/\text{Si}\) report [13]. It is well known that the relative dielectric constants for bulk \(\text{SiO}_2\) and \(\text{Y}_2\text{O}_3\) are 3.9 and 17.1, respectively. The present thin oxide (about 4 nm, estimated from the change in \(C\)) could contribute to decreasing the measured value of \(\varepsilon_r\) as the RTP temperature increasing from 700 to 850 °C.

C–V studies of the films were also performed at a frequency of 1 MHz with a small signal of 10 mV amplitude while the d.c. voltage of the top Al electrode was swept from a negative to a positive bias and back again. Fig. 4 shows the C–V plots for a 225 nm thick \(\text{Y}_2\text{O}_3\) film after RTP at 850 °C as compared with that of the as-deposited film. It is observed that there still exists a hysteresis phenomenon for the as-deposited film, while the RTP-treated sample shows a nearly ideal capacitor behavior. The observed hysteresis behavior could result from the interface states attributed to the difference between the structural properties of polycrystalline \(\text{Y}_2\text{O}_3\) and Si substrate. The X-ray measured data (as shown in Fig. 2) can confirm the inference because the \(\text{Y}_2\text{O}_3\) film after RTP has the tendency to recrystallize based on the Si substrate. This indicates that the interface states between \(\text{Y}_2\text{O}_3\) and Si can be apparently improved by RTP.

Another important feature for an insulator to be used in the EL structure is its electrical properties. The effect of RTP on the electric properties of \(\text{Y}_2\text{O}_3\) films was investigated by measuring the diodes in the accumulation mode with the top Al contact biased negatively. An I–V characteristic for the \(\text{Y}_2\text{O}_3\) film (the same sample described in Fig. 4) after RTP at 850 °C is depicted in Fig. 5. The observed leakage current density at an applied electric field of 1.8 MV cm\(^{-1}\) was about 3 \(\times\) 10\(^{-8}\) A cm\(^{-2}\). It is worth mentioning that the electric breakdown of the film is not observed as the electric field increases up to 4.4 MV cm\(^{-1}\) in all samples. These values
Fig. 6. Leakage current of Y$_2$O$_3$ as a function of RTP temperature. Arrow indicates the leakage current of the as-deposited film.

are superior to those reported for Y$_2$O$_3$ films annealed by a conventional furnace [13,14]. Fig. 6 illustrates the leakage current density of Y$_2$O$_3$ as a function of the RTP temperature. The measured leakage current density decreases considerably with increasing RTP temperature, and shows one order of magnitude lower than that of the as-deposited sample. Under such a high electric field, the effect of the intermediate oxide formed by RTP can be ignored since the oxide is thin (about 4 nm) and the injected carriers having sufficient energy can tunnel through. The reduction of leakage current after RTP could be understood in terms of improvements of crystal quality and interface states, which agrees well with the X-ray and C-V results.

4. Conclusions

High-quality Y$_2$O$_3$ films on Si(100) substrates were obtained by r.f.-magnetron sputtering combined with the RTP treatment. The crystallinity of the as-deposited films, strongly oriented to their (111) axis of cubic structure, was found to be improved and exhibit the (400) orientation after RTP. The result suggested a recrystallization process occurs based on the (100) Si substrate. The dielectric constant decreases and the leakage current density can be reduced to $3 \times 10^{-8}$ A cm$^{-2}$, which is lower one order of as-deposited samples. Up to 4.4 MV cm$^{-1}$ electric field, no breakdown behavior was observed in all samples. These results suggest that the RTP technology can improve the dielectric and electrical properties of the Y$_2$O$_3$ films and is suitable for EL and integrated Si-based devices.

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