# Low interface states and high dielectric constant $Y_2O_3$ films on Si substrates

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$Y_2O_3$ films were deposited on $c$-Si substrates at temperatures in the 400–550 °C range, with no further thermal treatment given to these samples, using the spray pyrolysis technique. The spraying solution was yttrium acetilacetonate disolved $N,N$-dimethylformamide. In addition, a solution of $H_2O-NH_4OH$ was sprayed in parallel during the deposition process to improve the optical, structural, and electrical properties of the deposited films. The growth of a $SiO_2$ layer between the yttrium oxide and the Si substrate during this deposition process resulted in interface state density values as low as $10^{10}$ $eV^{-1}$ $cm^{-2}$. An effective refractive index value of 1.86, and deposition rates close to 1 Å/s were obtained. The $Y_2O_3$ films were polycrystalline with a crystalline cubic phase highly textured with the (400) direction normal to the Si surface. An effective dielectric constant up to 13, as well as a dielectric strength of the order of 0.2 MV/cm was obtained for ~1000 Å thick as-deposited films incorporated in a metal-oxide-semiconductor structure. © *2006 American Vacuum Society.* [DOI: 10.1116/1.2214710]

## I. INTRODUCTION

High-$\kappa$ dielectric thin films are being studied for a variety of applications. Several materials have been studied for this purpose. In particular, metal oxides such as $ZrO_2$, $HfO_2$, $Al_2O_3$, as well as rare-earth oxides such as $Y_2O_3$, $La_2O_3$, $Pr_2O_3$, and $Gd_2O_3$ have been proposed to replace $SiO_2$ because their high dielectric constant ($10<\kappa<30$), thermal stability, a relatively high conduction band offset, and a high dielectric breakdown.[1] Yttrium oxide ($Y_2O_3$) has a dielectric constant between 14 and 18,[2] a high crystalline stability[3] and mechanical strength,[4] and a high refractive index ($n \cong 2$).[5] Epitaxial growth of rare-earth oxides has been reported to be achieved using molecular beam epitaxy (MBE).[6] Several other deposition methods have been used to obtain $Y_2O_3$ thin films, such as pulsed laser deposition,[7] rf-magnetron sputtering,[8] spray pyrolysis,[9] and sol gel.[10] In the present work we report the deposition and characterization of $Y_2O_3$ thin films obtained by ultrasonic spray pyrolysis. These films were deposited from a spraying solution of yttrium acetilacetonate [Y(acac)$_3$] in $N,N$-dimethylformamide ($N,N$-DMF). The mist of a second spraying solution, consisting of a mixture of $H_2O-NH_4OH$, supplied simultaneously, and in parallel to the yttrium spraying solution, improved dramatically the optical, structural, and dielectric properties of the $Y_2O_3$ films. Specifically, the formation of a high quality interfacial layer of $SiO_2$ improved the interface characteristics with the silicon substrate.

## II. EXPERIMENTAL PROCEDURE

The ultrasonic spray pyrolysis technique was used to deposit the $Y_2O_3$ films on $c$-Si wafers with (100) orientation and low resistivity or (111) and high resistivity, for electrical and optical measurements, respectively. The silicon wafers were previously cleaned with a well established procedure.[11] Spray pyrolysis is considered a simple and low cost deposition method for film deposition. This technique has been used to obtain high quality metallic oxides.[12–15] It consists of an ultrasonic generator used for mist production from a spraying solution containing the proper reactive materials. The mist is transported through a glass tube to the substrate surface which is being heated to achieve a pyrolytic chemical reaction. This deposition process is performed in an atmospheric pressure air ambient. In this work, a 0.03 M yttrium spraying solution was prepared by dissolving Y(acac)$_3$ in $N,N$-DMF, from Alfa AESAR and J.T. Baker, respectively. In addition, the mist of a second spraying solution, consisting of a mixture of $1H_2O-1NH_4OH$ (J.T. Baker), was also carried, during the deposition process, to the surface of the silicon wafers, used as substrates. The mists of both spraying

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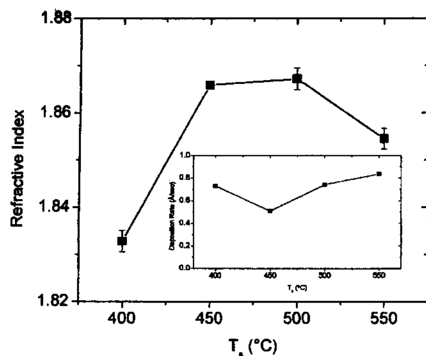


FIG. 1. Refractive index as a function of the substrate temperature for the films of $Y_2O_3$. The inset shows the deposition rate of the films as a function of the substrate temperature.

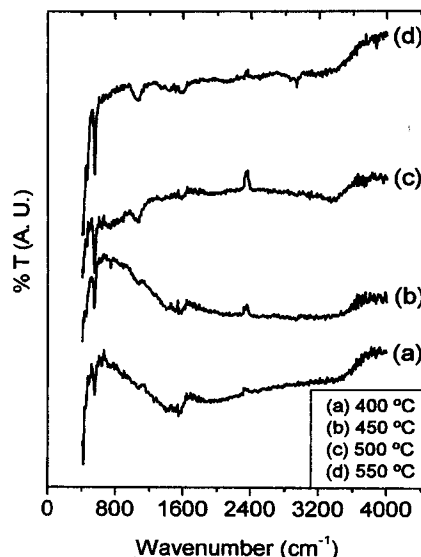


FIG. 2. IR spectra of the $Y_2O_3$ films deposited at different substrate temperatures.

solutions were obtained by means of two commercial ultrasonic humidifiers (operated both at 0.8 MHz). High purity air was used as carrier gas at flow rates of 10 and 3 lpm, for the yttrium and the $H_2O-NH_4OH$ spraying solutions, respectively. A molten tin bath, whose temperature was electronically controlled, was used as substrate heating system. The films were deposited at substrate temperatures of 400, 450, 500, and 550 °C.

The as deposited films were characterized in a Gaertner LSE Stokes Ellipsometer (632.8 nm), a Nicolet infrared spectrometer, a digital instruments atomic force microscope, and a Siemens D-5000 x-ray diffraction system, using a Cu $K\alpha$ radiation (0.154 06 nm). A selected group of $Y_2O_3$ films were integrated in metal-oxide-semiconductor (MOS) structures defined by thermally evaporated aluminum dots (0.011 or 0.0035 $cm^2$) on top of the films. The capacitance and current versus voltage characterizations were performed with a commercial equipment supplied by Keithley using the Model 82-DOS Simultaneous CV program.

## III. RESULTS AND DISCUSSION

Figure 1 shows the refractive index of the $Y_2O_3$ films as a function of the substrate temperature. The highest refractive index value observed was 1.87. These refractive index values compare well with those reported for high quality good density $Y_2O_3$.[5] Also the at. % ratio of Y to O, as measured by energy dispersion spectroscopy (EDS), was found to be 2:3 within the accuracy of the EDS technique. The inset in this figure shows the behavior of the deposition rate. The films thicknesses were about 1000 Å in this case, and the average deposition rate was in the 0.5–0.9 Å/s range, having no clear dependence with the substrate temperature. Our deposition rates compare favorably with those reported for epitaxial $Y_2O_3$ layers grown at 450 °C by e-beam evaporation under ultrahigh vacuum conditions (0.5–0.7 Å/s).[16]

Figure 2 shows the IR spectra of the $Y_2O_3$ films deposited at the different temperatures. The spectra show the characteristic $Y_2O_3$ bands at 557 and 459 $cm^{-1}$.[17] The sharpness and intensity of these bands is larger when the films are deposited at higher temperatures (500 or 550 °C). Also, a $SiO_2$ related peak at approximately 1145 $cm^{-1}$ is observed at these temperatures, indicating that a thin $SiO_2$ oxide layer at the Si substrate interface has been formed. This is due to the fact that the spray pyrolysis deposition technique is performed in an open atmospheric pressure air ambient. This observation is consistent with previously reported work using transmission electron microscope (TEM) where, under similar deposition conditions, a thickness of an $SiO_2$ layer up to 50 Å (Ref. 13) is formed at the silicon interface. In general, it is difficult to obtain films deposited on silicon without the appearance of $SiO_x$, even in systems which use high vacuum conditions,[16] although the electrical quality of these films is in general poor when the oxide is formed at low temperatures. A slight decrease of the $SiO_2$ related peak is observed as the substrate temperature during deposition is reduced. Carbon related peaks were also found at 1500 and 1410 $cm^{-1}$.[17] The carbon content in the films might be due to an incomplete decomposition of the Y(acac) reactant and/or the *N*,*N*-DMF solvent. These carbon related peaks decrease for films deposited at high temperatures (500–550 °C). In addition, a reduced but noticeable content of –OH groups or absorbed water related bands at 3460 and 1650 $cm^{-1}$ were observed. These results suggest a high structural quality of the films that seems to be promoted by the addition of the $H_2O-NH_4OH$ mist. $Y_2O_3$ films deposited without it have, in general, poor structural quality.

X-ray diffraction patterns of the films show their polycrystalline nature (Fig. 3). A cubic phase (400) preferred orientation is observed as the substrate temperature of the films is increased (according to the JCPDS 43-1036 diffraction card). Also the (622) diffraction peak was observed, but with lower intensity, at high temperatures (500 and 550 °C). At 400 °C, the (222) peak is the strongest. Previous work, established that heteroepitaxial growth at 450 °C results in a (110) preferential orientation.[16] Also, $Y_2O_3$ films deposited by e-beam evaporation at substrate temperatures of 270 °C show a (222) preferential orientation.[18]

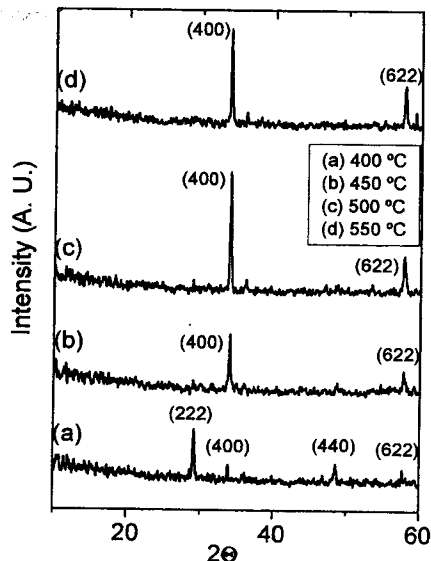


FIG. 3. X-ray diffraction patterns of the films deposited at different substrate temperatures.

Figure 4 shows the typical morphology of the films as observed by atomic force microscope (AFM) on a film deposited at 500 °C, where a high degree of texturing can be appreciated. This type of morphology was observed only when the films were deposited with the addition of the $H_2O$–$NH_4OH$ mist. Similar degree of texturing has been reported for $Y_2O_3$ films deposited by e-beam evaporation.[18] The average root mean square surface roughness was in the range of 40–60 Å. A low surface roughness is in general an stringent requirement for applications required in the microelectronic industry.

Figure 5 shows a high and low frequency capacitances versus voltage curve obtained on a capacitor prepared with a film that was deposited at 500 °C with an effective thickness of 879 Å as measured by single wavelength ellipsometry. From the capacitance value at the accumulation region, the effective dielectric constant ($\kappa$) of the $Y_2O_3$ films can be

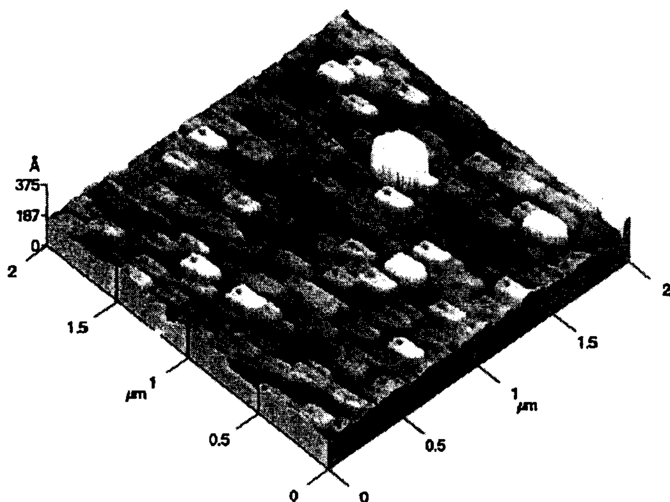


FIG. 4. Typical AFM image obtained on a film that was deposited at 500 °C.

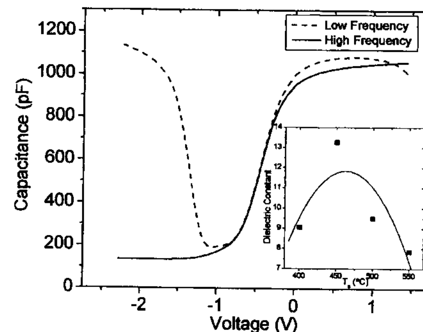


FIG. 5. High and low frequency capacitances vs voltage for a film deposited at 500 °C. The inset shows the dielectric constant as a function of the substrate temperature found in the films.

obtained, according to the following equation $C=\kappa\varepsilon_o A/d$. The inset in Fig. 5 shows that the dielectric constant reaches a maximum value of 13.3, when films are deposited at 450 °C. Films deposited at 400, 500, and 550 °C show in average a lower dielectric constant (~8.8). This behavior seems to be a result of competing effects produced with increasing deposition temperatures, in one hand a better overall quality $Y_2O_3$ film and on the other hand, the formation of a thicker interfacial $SiO_2$ layer.

In order to estimate the role of the interfacial oxide layer, a set of MOS devices were fabricated with yttrium oxide layers deposited at 450 °C having an effective thicknesses ($d_{\mathrm{eff}}$) of ~202 and 417 Å. The effective dielectric constant decreased down to 6.9 for the thinnest layer. Assuming that the deposited layer is integrated by a constant thickness oxide layer of $SiO_2$ forming a series capacitance with the yttrium oxide layer on top, a linear fit to the $\varepsilon_o A/C_{\mathrm{Ox}}$ versus effective thickness ($d_{\mathrm{eff}}=d_{\mathrm{SiO_2}}+d_{\mathrm{Y_2O_3}}$), yielded an $SiO_2$ thickness of ~80 Å (considering $k_{\mathrm{Ox}}=3.9$), and a dielectric constant for the yttrium oxide layer of ~11.4. This oxide thickness was similar to the one estimated by ellipsometry (~67 Å) using 1.46 value for the refractive index of the SiO2 layer in the analysis for double transparent layers on a silicon substrate.

Figure 6 plots the interface trap density ($D_{\mathrm{it}}$) as a function of the silicon energy band gap obtained from the *C-V* data shown in Fig. 5. The $D_{\mathrm{it}}$ near midgap is in the low $10^{10}$ $\mathrm{cm^{-2}\,eV^{-1}}$ range, comparable to those values reported for good quality thermal $SiO_2$ on Si (Ref. 19) grown at higher temperatures. The inset in Fig. 6 shows the behavior of the interface state density at midgap for the films as a function of the substrate temperature during deposition. The interface trap density for films deposited at 550 °C is not included because it was not possible to measure it. Low interface state density is an indication of a high quality interface.

Table I reports the electrical parameters calculated for the MOS diodes. *C-V* curves are slightly shifted to the left, indicating a positive charge in the films. The maximum flatband voltage shift $V_{\mathrm{fb}}$ (−1.02 V), occurs for the films deposited at 450 °C. The minimum effective oxide charge concentration $N_{\mathrm{eff}}$ is in the high $10^{10}$ $\mathrm{cm^{-2}}$ range. This value

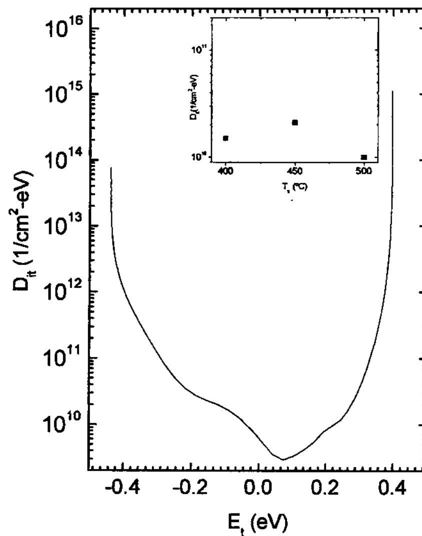


FIG. 6. Interface trap density as a function of the energy silicon bandgap for the film deposited at 500 °C. The inset shows the interface trap density for the films deposited as a function of the substrate temperature.

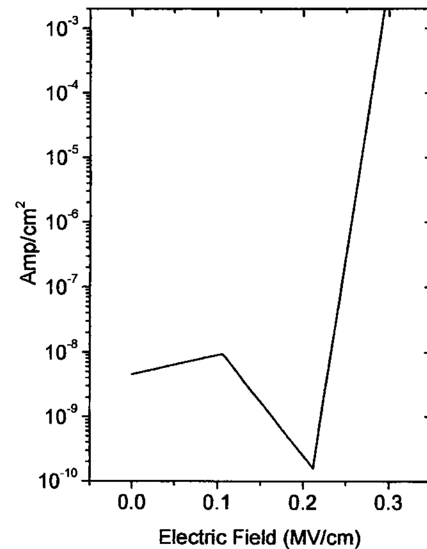


FIG. 7. Current density vs electric field for a film that was deposited at a substrate temperature of 450 °C.

is present in films deposited at 500 °C. The lowest interface trap density near midgap also appears in films deposited at 500 °C. An interface trap density of $1.0\times 10^{10}$ cm$^{-2}$ eV$^{-1}$ is found for these films.

Finally, a typical current density versus electric field characteristic is shown in Fig. 7, for the MOS structure incorporating a film deposited at 500 °C. In general, a poor $J$-$E$ response is obtained in the films with a dielectric strength ($E_{max}$), lower than 0.2 MV/cm. It has been suggested that $E_{max}$ is strongly related to the structure of the films, amorphous films are better candidates than polycrystalline materials to have a high dielectric strength. In the present case, the polycrystalline nature of the $Y_2O_3$ films as well as the observed surface roughness might be responsible for the relatively poor dielectric strength observed, even though the thin silicon oxide layer formed at the interface, is most likely, amorphous.

The results above described suggest that the $NH_4OH$–$H_2O$ mist plays an important role in achieving the growth of a high quality silicon oxide at the Si substrate interface, reducing density of interface states and the carbon related contamination. It also seems to induce a film deposition with a preferred (400) crystalline orientation of the cubic $Y_2O_3$ phase for temperatures above 450 °C. However, the exact nature of the $NH_4OH$–$H_2O$ role still has to be determined. Previous work has shown that $NH_3$ and $N_2O$ annealing of $Si_xN_y$ films reduce their leakage current density.[1] On the other hand, it has been found that the use of ammonia converts a hydrogen-terminated silicon surface to a surface covered with a monolayer of nitrogen. Nitridation of silicon surfaces has been shown to be effective as a dry chemical process for preparing uniform Si surfaces terminated with specific atoms or molecules other than hydrogen.[20] It is possible then, that the $NH_4OH$ decomposes in $NH_3$ and $H_2O$ during the deposition process and favors a nitrogen terminated Si surface which in turn leads to a high quality silicon oxide layer at the interface with a low interface trap density.

## IV. CONCLUSIONS

$Y_2O_3$ films were deposited on $c$-Si, using the ultrasonic spray deposition technique. The addition of $NH_4OH$–$H_2O$ mist during the deposition process improved, in general, the $Y_2O_3$ films quality and the electrical characteristics of a thin (~80 Å) interfacial $SiO_2$ layer that grows between the yttrium oxide and the silicon substrate during the deposition process. Dense and clean films were deposited with a high degree of texturing of the cubic $Y_2O_3$ phase on the (400) preferred orientation normal to the substrate. The MOS structures fabricated with these films as dielectric layer, have an effective dielectric constant up to 13, and with an interface trap density in the low $10^{10}$ cm$^{-2}$ eV$^{-1}$ range.

TABLE I. Electrical parameters of the MOS diodes.

| $T_s$ (°C) | $\kappa$ | $D_{it}$ ($\times 10^{10}$ cm$^{-2}$ eV$^{-1}$) | $V_{fb}$ (V) | $N_{eff}$ ($\times 10^{11}$ cm$^{-2}$) | $E_{max}$ (MV cm$^{-1}$) |
|---|---|---|---|---|---|
| 400 | 9.1 | 1.5 | −0.75 | 2.9 | <0.2 |
| 450 | 13.3 | 2.1 | −1.02 | 6.7 | <0.2 |
| 500 | 9.5 | 1.0 | −0.48 | 0.68 | <0.2 |
| 550 | 7.9 | | | | <0.2 |

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