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Optical characterization of polysilazane based silica thin films on silicon substrates

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ABSTRACT

In this work polysilazane based silica thin films grown on multilayer structures of different ultra-thin barriers (UTBs) on silicon substrates were studied. The silica thin films were obtained by polysilazane spin coating deposition (also called SOD, spin-on dielectrics) upon different UTB liners (silicon nitride or silicon dioxide). By curing the SOD with thermal treatments the polysilazane is converted into silica thin films. The degree of conversion to SiO_2 was analyzed and the oxide local structure was studied in terms of Si—O—Si bridges by FTIR spectroscopy. Steady state and time resolved luminescence were applied to further characterize the oxide structure, the substrate–silica interfaces and the presence of defects. The analysis revealed the presence of dioxasilirane, $=Si(O_2)$, and silylene, =Si:, defect centers in the samples grown on silicon nitride UTB, while these defects are not observed in samples grown on silicon oxide UTB.

1. Introduction

In the spite of Moore's Law, ultra-large-scale integrated (ULSI) circuits require an increasing density of devices every new generation of circuits. Due to the continuous decrease in the dimensions and spacing of devices on integrated circuits (ICs), insulating layers (typically SiO_2) have to be deposited to electrically isolate the different active components of the circuit (transistors, resistors, capacitors). Indeed the architecture of the circuits plays a key role and insulating structures such as shallow trench isolation (STI) regions are formed in trenches within the substrate between components. Such trenches can have a width of about 50 nm or even smaller, and filling such narrow gaps can be challenging [1,2]. In addition, the dielectric material must be able to withstand subsequent processing steps such as etching and cleaning steps.

Spin-on dielectric (SOD), that is the deposition of specific silica precursors by spin coating, represents a valid alternative to high density plasma or other techniques based on chemical vapor deposition (CVD), in particular regarding the demand of gap-filling in STI with aspect ratio greater than 5:1 [3–7]. Indeed flowable materials with high gap filling properties such as SOD and spin-on polymers like silicates, siloxanes, silazanes or silisesquioxanes, have been recently developed [5,6,8,9].

Dealing with SOD materials, the key point is the chemical physical quality of the obtained insulating layer: the silica conversion degree by thermal treatment with furnace has to guarantee a reliable oxide in terms of density, robustness and resistivity to breakdown [10]. Increasing furnace annealing temperature gives good results on flat wafers in terms of material conversion degree, but it seems to have not the same impact concerning the filling of narrow trenches [11].

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Table 1
List of analyzed samples and parameters growth of the UTBs.

Sample name	Furnace atmosphere	Pressure (Pa)	Temperature (°C)	Treatment time (min)
O1	$N_2 + O_2$	Atm.	1000	300
O2	$N_2O + SiH_4$	66.6	790	180
N1	$NH_3 + SiH_2Cl_2$	40	775	110

The effect of the substrate composition on the properties of thin layer was recently studied [12], similarly, in this work we focus our attention on the ultrathin barrier (UTB) deposited between the active areas and the insulating dielectrics and how different UTBs can affect the silica conversion of selected polysilazane based SOD. We present a FTIR analysis of the silica converted SOD as a function of different UTBs (silicon nitride and silicon oxide), after furnace curing, focusing on the effective silica conversion in terms of SOD bulk properties. The optical properties were studied by steady state and time resolved photoluminescence (PL) in order to assign the nature of defects at the SOD layer and to correlate the results of the different experimental techniques.

2. Material and methods

Polysilazane based SOD thin films were spinned on large high purity circular p-silicon mono-crystal wafers (diameter 200 mm), with (1 0 0) orientation. Different ultra-thin barriers (UTB) of silicon nitride or silicon dioxide, each one with thickness less than 80 nm, were deposited as substrate liners upon silicon wafer by thermal treatment inside a furnace in different chamber atmospheres ($N_2 + O_2$, $NH_3 + SiH_2Cl_2$ and $N_2O + SiH_4$), see Table 1 for details. Polysilazane was deposited on top of UTBs of the silicon wafer by spin coating, then a first bake treatment was performed in an inert atmosphere at 150 °C for 180 s in order to remove the solvent. A three step curing procedure was applied for all the samples: a first step at 400 °C (30 min) followed by 700 °C (30 min), both in a steam atmosphere and finally a 900 °C (30 min) in a dry atmosphere. Samples with SOD thickness of about 290 nm were obtained (the thickness was estimated by interferometric analysis).

Time resolved photoluminescence (TR-PL) measurements were performed with excitation provided by an optical parametric oscillator with a frequency doubler device (Spectra Physics MOPO), excited by the third harmonic of a pulsed Nd-YAG laser (Spectra Physics QuantaRay PRO-270), with pulse width at half maximum of 8 ns and 10 Hz of repetition rate. The PL signal was dispersed by a spectrograph (ARC-SpectraPro 300i) with a spectral bandpass <2.5 nm and detected by a gateable intensified CCD (PI MAX Princeton Inst.). Spectra were corrected for the optical transfer function.

FTIR measurements were performed in the 2500–400 cm^{-1} spectral range by using a FTIR spectrometer Nicolet Eco1000 model with a spectral resolution of 4 cm^{-1}.

The list of samples and the UTBs growth parameters are reported in Table 1.

3. Results

Fig. 1a reports the FTIR spectra of the different ultra-thin layers before SOD spin coating process. Both O1 and O2 samples display the FTIR spectrum of pure silica, with typical absorption peaks of Si—O bonds occurring at about 1080 cm^{-1} (stretching mode region), at 456 cm^{-1} (rocking mode region) and at 810 cm^{-1} (bending mode region) [13,14]. The FTIR spectrum on sample N1 presents two main bands at 830 cm^{-1} and 490 cm^{-1} which can be ascribed to Si—N vibration and to Si breathing vibrations, respectively [10,15].

Fig. 1b reports the spectra of the samples after SOD spin coating and curing by thermal annealing in different atmosphere: the main

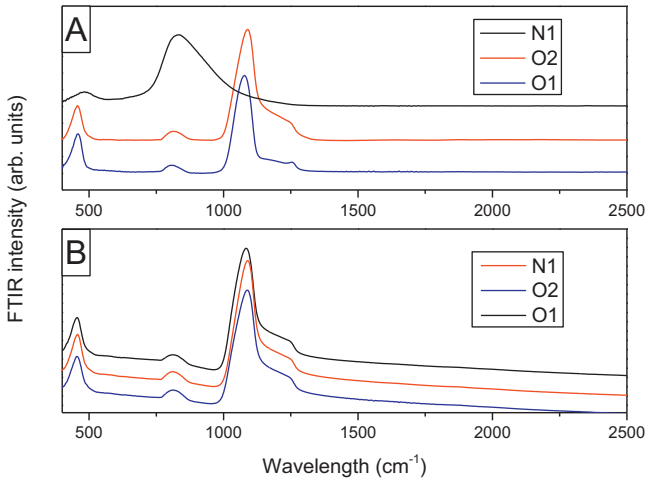

Fig. 1. (a) FTIR spectra of the ultra-thin layer before SOD spinning process. (b) FTIR spectra after SOD spinning process and thermal annealing.

vibrations of pure SiO_2 oxide are clearly observable for the whole set of samples. However, small differences in the FTIR spectra can be evidenced mainly in the region of the Si—O stretching mode; an enlarged view (900–1300 cm^{-1}) is reported in Fig. 2a. In this region the spectrum is dominated by the vibration of the Si—O—Si bridges and can be deconvoluted by assuming four Gaussian contributions: two main components, peaked at about 1050 cm^{-1} and 1090 cm^{-1} and two larger and less intense bands at 1150 and 1230 cm^{-1}. The four bands pertain to Si—O—Si vibrations in different local environments, as reported in the discussion section [14,16,17]. Fig. 2b reports the experimental data, the four Gaussian bands and the fit result (square correlation factor $R^2 > 0.98$). The fitting results are summarized in Table 2. The fitting procedure assumes as initial parameters the values reported in the literature for each band (see Table 1 for the assignment) [18–21] and it was performed, constraining the parameters of the fit of each curves to vary less than 10 cm^{-1} and 5 cm^{-1} for the center wavenumber and the FWHM, respectively.

In Fig. 3 the emission spectra recorded by exciting the different samples at 250 nm and gathered in the same experimental conditions are reported. Both the PL spectra from O1 and O2 samples present two maxima with relative low intensity, peaked at 295 (310) and 375 (392) nm in the O1 (O2) case (inset of Fig. 3). In the O2 case the overall PL intensity is larger than in the O1 case. Concerning

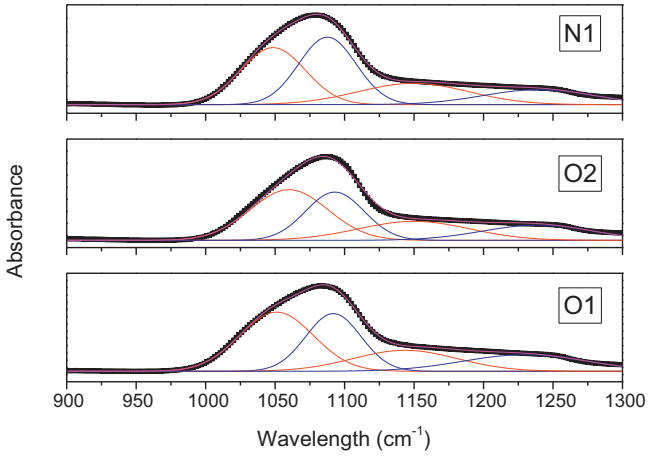

Fig. 2. FTIR spectra in the region of the SiO stretching mode (900–1300 cm^{-1}) and related fitting results: in red the deconvoluted contribution form bulk Si—O—Si bridges, in blue the deconvoluted contribution from boundary Si–O–Si bridges.