Evolution of Oxide and Oxynitride Absorption band in CMOS Gate Dielectrics as Studied by Ultraviolet Spectroscopic Ellipsometry

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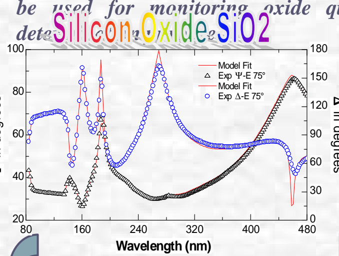
Abstract: Optical characterization needs for microelectronic materials, expand the spectral range of spectroscopic Ellipsometers toward the ultraviolet and even vacuum ultraviolet photon energies. This development is today clearly identified as well, in the very thin layer metrology. In the metal-oxide-semiconductor technology, with gate oxide thickness below 2nm-thickness, the control of the interfacial layer becomes a key point. If the spectral range limits given from today's instruments remain below 9 electron volt (ev), more interest can be found toward higher photon energies up to 11.3ev (110nm), when silicon substrate becomes mostly reflecting (n~0, k>0). In this case, one obtains direct optical constant of many materials useful in Microelectronics such as lithography resists. Particularly in that photon energy range, spectroscopic ellipsometry data, for different thin gate oxides and oxynitride are reported. The effects of the oxidation temperature, thickness or nitridation-processing are presented. The trend is to demonstrate that position and shape of the ultraviolet absorption band could be used for monitoring oxide quality as well as for SiO_xN_y *stoechiometry determination.*

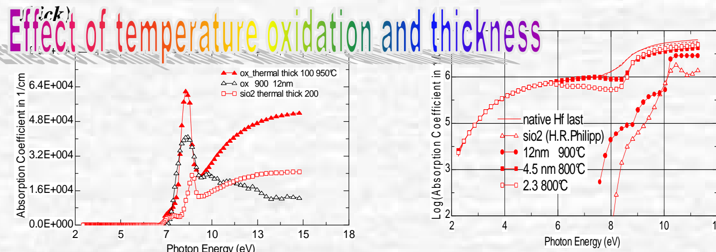
Silicon Oxide SiO2



sio2_900c Optical Constants

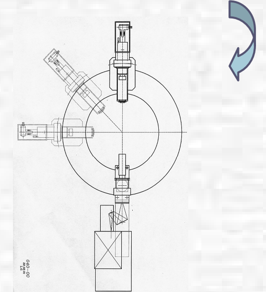
Experimentally observed optical constants, n and k, corresponding to a 950°C-reference, 104nm-thick, wet thermal oxide, are shown here, where the optical indices n and k have been extracted from SE measurements. The absorption peak seen at 8.50 eV corresponds to the excitonic relaxation process present in the oxide. Compared to literature v-SiO2 data, the onset of the Urbach absorption edge of SiO2, an exciton–phonon like peak, appear at a much higher value (10ev.). In order to differentiate oxides, it is convenient to reproduce their respective absorption coefficient α*. The same 104nm-thick thermal oxide case is plotted together with a 12nm-thick thin 800 °C grown oxide. In both cases, the magnitude of* α *is much less compared to the vitreous* SiO_2 *silica values.. Nevertheless, a 800°C oxidation temperature the thin 12nm-thick oxide has a lower intensity and gives a peak in absorption at the same position similarly to the reference samples (100nm and 200nm-thick).*

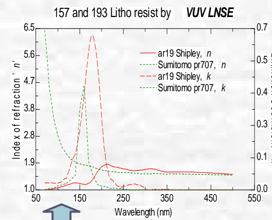
Effect of temperature oxidation and thickness



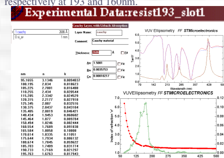
The respective logarithm of α are reported: Thin oxide samples are i) a native oxide, a through an *HF last* sequence cleaned and left several days in atmospheric ambient, ii) a 2.3nm-thick 800°C, iii) a 800°C 4.5nm and 12nm -thick thin oxides. The upper limit is given by Philipp's data. Significant differences exist between each of these oxides. With the native oxide sample, a SiO_x radicals contribution is the plateau effect (curve HF last, i.e. upper filled circles curve) in the region below 8 ev (α~10^5 cm^{-1} and then a continuous increase is observed with α~ $5 10^6$ cm^{-1}). The 2.3nm-thick oxide can be seen mainly as a sub-oxide material with a probable presence of many oxygen deficient centres, belonging to the structural transition layer from the silicon oxide interface. Incompletely linked clusters of SiO_x tetrahedra in the first few mono-layers from the interface, quench any phonon relaxation mechanism. With the 800°C (empty circles and empty and filled square curves) thin oxide samples, intermediate situations are observed. Following the oxidation conditions, different behaviours appear in spectral region where the Urbach absorption edge should be clearly pronounced. Below, still exists a plateau originated from a non-stoechiometry SiO_x dielectric and a defects contribution with an absorption level of the same order of magnitude.

Ultraviolet variable angle Spectroscopic Ellipsometer: Experimental set-up





Analysis of two lithography resists demonstrating the overall spectral range of the instrument. Only the optical constant n, k extracted from the tan Ψ and cos Δ measured in the range 80 to 500nm are reported. The Ar19 is from Shipley (antireflective coating) and Sumitomo PR707 193 nm lithography resist. Absorption peaks are clearly rising respectively at 193 and 160nm.



Detailed SE analysis for the 193nm resist

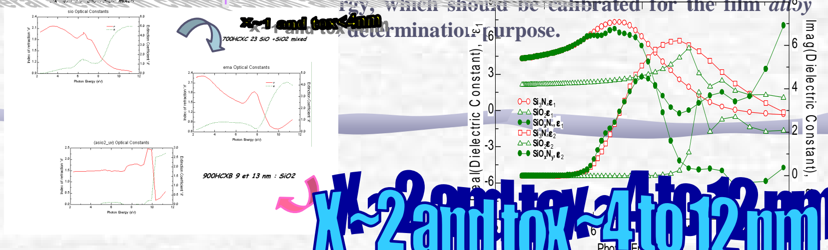
Experimental Details: the v-uv spectroscopic ellipsometer.

A variable angle, rotating polarizer spectroscopic ellipsometer was built in the laboratory, giving access to a wide v-uv, uv-visible (100-600nm) spectral range and using a patented low noise detection concept [7]. The ellipsometer is inside a continuously nitrogen flow purged N_2 box that eliminates the absorption of v-uv radiation by ambient air. Such a spectral range is covered by switching two detectors: one for the visible range (180-600nm) and the other dedicated to the v-uv range (100-200nm). The optical components are all coated with magnesium fluoride ($AlMgF_2$), thus reducing reflection losses in the instrument's optical path between the source and the detectors. The polarizer and analyzer are Rochon MgF_2 bi-prisms ensuring perfect transparency in the ultraviolet range even below 110nm. We use a concave holographic, 250nm blazed with 1200 Al grooves/mm grating monochromator. The source is a 30-watt, MgF_2 windowed deuterium lamp. Photon counting is processed with a multiscaler acquisition module. Data can be acquired simultaneously on two inputs while sampling is done over for several periods. Measurements were made at a 75° incidence angle in order to enhance the well-known visible range Brewster transition, increasing the accuracy of thickness determination. Nevertheless, checks were made using other incidence angles in order to ensure general consistency. Being less sensitive to the substrate, in the high-energy range, the optical indices n, k can be directly extracted by numerical inversion from the D, Y ellipsometry angles.

NH3 nitridation and oxynitrides.

For oxynitrides, vuv spectroscopic ellipsometry affords also a full potentiality in stoechiometry evaluation. Previous study has demonstrated in the visible range that the technique could be used in order to analyze the nitroxide SiO_xN_y film composition through the random bonding model (RBM). Unfortunately , there remains for thin layers very often correlation between parameters leaving the problem partially solved. Although no complete analysis with several x, y composition values has been yet carried out in the v-uv range, primary results show that the measured n, k values fall fairly well in between the expected basic component limits, i.e., Si_3N_4 and SiO_2. This is illustrated here.There are measurements in the case of an only 6nm-thick oxynitride sample, which has been checked for its in-depth homogeneous composition. The extracted dielectric function (real and imaginary part) ε_1 and ε_2 (filled circles lines) are shown together with the corresponding dielectric function of Si_3N_4 (empty square and circles curves) and that of SiO_2 (empty triangles curves). A shift of the maximum of ε_2 for the oxynitride is observed toward a lower energy, which should be calibrated for the film alloy determination purpose.

General trends in composition and thickness evolution



In the v-uv, the Urbach absorption process certainly follows as well, the reordering of the interface from SiO_x toward the organized S