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Thickness determination of very thin SiO_2 films on Si by electron-induced x-ray emission spectroscopy

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Electron-induced x-ray emission spectroscopy (EXES) associate with a semi-empirical electron scattering model is used to determine thicknesses between 2 and 21 nm of SiO_2 films on Si. The small charging effect occurring upon electron irradiation is taken into account by introducing a retarding potential in the model. The results are in very close agreement with those obtained by spectroscopic ellipsometry and x-ray reflectometry. It is demonstrated that the EXES with its model is a well-suited method for the quantitative analysis of thin insulating films with an uncertainty lower than 5%. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1511281]

The new generation of electronic devices has led to the down-scaling in the dimensions of the complementary metal–oxide–semiconductor (CMOS). This down-scaling requires accurate quantitative measurements with depth resolution of a few nanometers or better. There is only a small number of techniques[1–3] with such a resolution. Most of the surface techniques use electrons as incident or detected particles, because of their continuous slowing down in the matter and their short path relative to photons. In such cases however, these techniques become sensitive to the charging effect, and the analysis of insulating sample can be difficult.[1] We propose to use the electron-induced x-ray emission spectroscopy (EXES) associated with a semi-empirical electron scattering model taking into account the charging effect to perform high depth resolution quantitative analysis of very thin SiO_2 films on Si. We compare our results with those obtained by spectroscopic ellipsometry and x-ray reflectometry to demonstrate the good performances of the EXES method.

The EXES is a nondestructive technique in which the sample is irradiated by an electron beam. Following the ionization of the analyzed element, characteristic x-rays are emitted. By increasing the electron energy from the ionization energy E_s up to several times this energy, the analyzed thickness (i.e., the thickness for which primary electrons have an energy greater than the emission threshold energy) can be varied from a few nanometers (i.e., the surface zone) up to a depth of several hundreds of nanometers. This enables us to probe samples with inhomogeneous depth.

The quantitative interpretation of the x-ray intensity requires appropriate models for describing electron–matter interaction. The aim of these models is to reproduce the in-depth distribution of the ionizations in a wide range of electron energies. Previous quantitative models do not permit good performances in the low electron energy ($\leqslant 5$ keV) and low overvoltages ($E_0/E_s \leqslant 1.2$) used in our case. In order to operate in these conditions, a simulation model for the low energy electron region at high depth resolution was developed.[4,5] In this model the target is cut in imaginary slices along planes parallel to the sample surface. Electrons crossing such an elementary layer of thickness dz, located at depth z, are scattered back and forth between two virtual planes. The depth distribution of the ionizations in this elementary layer results in the sum of the contribution of all the electrons that are transmitted, backscattered, and transmitted a second time. The model takes into account the physical parameters that describe the electron–matter interaction, such as the electron transmission and backscattering coefficients,[6] the electron energy[7] and angular[8] distributions, and the ionization cross sections.[9] It also takes into account the absorption of the outgoing photons in the sample. This model is used in order to carry out the quantitative analysis of homogeneous or stratified samples, pure or complex.[10]

When a nonconducting material is irradiated by an electron beam, charging phenomena can occur. An electric field is built up in the material by the electrons trapped below the surface, which can modify the parameters of the electron–matter interaction. The consequence is that the shape of the in-depth distribution function of the characteristic x-ray production is distorted.[11–13] The distortion is due to the fact that the retarding electric field induces a slowing down of the incident electrons and their deflection in the sample. This reduces the penetration depth. Thus, the charging effect induces changes in measurable quantities such as the backscattering coefficient and the x-ray signal. We have used the formalism developed by Cazaux[11] and assumed a steady charge distribution. The sample surface is irradiated with a beam whose dimensions are far larger than the maximum depth penetration z_m of the incident electron. In our analytical conditions, the irradiated sample surface is about 1 cm^2.

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Thus, the electric field depends only on the depth. The electric field built up inside the material is, according to Cazaux[11]

$$V=V_M\left[\left(\frac{z}{z_M}\right)^2-2\left(\frac{z}{z_M}\right)\right],$$

with

$$V_M=-F_M z_M/2,$$

where F_M is a constant and

$$z_M=C(E_0^n-E_s^n)/\rho,$$

where C is a constant, n is a constant which depends on E_0[14] and ρ is the density of the insulating material.

As we have seen, the major phenomenon is the slowing down of electrons, which decreases their penetration depth from z_M to z'_M. Thus, by introducing the retarding potential V_M in the former equation:

$$z'_M=C[E_0^n-(E_s+eV_M)^n]/\rho.$$

Note that this correction can be applied to the case of positive charging (accelerating potential) by changing the sign of V_M.

With the aim of studying the potential applicability of the EXES method, measurements of the x-ray intensity emitted by thin films of known composition are performed. The samples consist of SiO_2 films, 1.9, 9.5, 13, and 21 nm thick, produced by dry oxidation of silicon (111) single crystals. From the x-ray measurements and the electron scattering model, the thicknesses are determined and compared with those obtained by ellipsometry and reflectometry used as references.

The spectroscopic ellipsometry is widely used to control the thickness and the optical properties of thin films. In this method, the amplitude and phase changes of a polarized radiation are measured after reflection on the sample.[15]

Concerning reflectometry experiments, the optical constants of amorphous SiO_2 and Si have been calculated from reflectivity measurements as a function of the glancing angle θ. The data were derived using a recursion equation.[16,17] For a single layer (indicated by subscript ℓ) of thickness d and dielectric constant ϵ_ℓ located between the incident medium (vacuum indicated by subscript v) and an unbounded medium (semi-infinite substrate indicated by subscript s), the reflection coefficient is written

$$r_F=\frac{r_{v\ell}+r_{\ell s}\exp\left(2id\frac{\omega}{c}\sqrt{\epsilon_\ell-\cos^2\theta}\right)}{1+r_{v\ell}r_{\ell s}\exp\left(2id\frac{\omega}{c}\sqrt{\epsilon_\ell-\cos^2\theta}\right)},$$

where r_{ij} is the Fresnel coefficient at the interface between i and j and ω/c is the wave number in vacuum. According to the theory of Beckmann and Spizzichino,[18] the specular reflectivity of a sample with a statistical rough surface with a rms height of the surface roughness σ is

$$R=R_F\times\exp\left[-\left(2\frac{\omega}{c}\sigma\sin\theta\right)^2\right],$$

where R is reflectivity of the rough surface and $R_F=|r_F|^2$ is reflectivity of an ideally smooth surface. Experimentally one measures the reflectivity $R=|r|^2$. The angular dependent reflectivity spectra were evaluated by least-squares fits of the theoretical curves to the measurements by varying the following parameters: the dielectric constant, the rms roughness height and thickness of the SiO_2 film, the dielectric constant of the substrate, and the rms roughness at the interface between the substrate and film. In a first iteration, fits were carried out for which the film thickness, the values of the surface and interface roughness, as well as optical constants of the film, were varied. Thus the thickness of the film (see Table I) and the roughness could be determined. Finally, the optical constants of the film have been fitted again with fixed values for thickness and roughness.

TABLE I. Comparison of the thickness (in nm) of the SiO_2 films as determined from the simulation of the EXES experiments and by ellipsometry and x-ray reflectometry.

EXES	Ellipsometry	Reflectometry
1.9 ± 0.1	1.9 ± 0.5	1.90 ± 0.04
10.4 ± 0.2	9.5 ± 1.0	10.8 ± 0.2
13.0 ± 0.3	13.0 ± 1.0	13.0 ± 0.3
21.0 ± 0.6	21.0 ± 1.0	22.0 ± 0.4

The x-ray spectra are measured with a wavelength dispersive spectrometer[19] using a TlAP (001) crystal at the first reflection order. Excitation curves, that is, the intensity of the characteristic O K_α x-ray emission as a function of the incident electron energy E_0 from 0.53 up to 5 keV, are measured for the various SiO_2/Si samples. A beam current density of 1 mA/cm^2 is applied. The presented excitation curves are the accumulation of about four excitation curves with a 15 s acquisition time for each electron energy level. The stability of the x-ray intensity along these curves was carefully checked and no evolution has been detected. The intensity of the O K_α emission of a 120-nm-thick SiO_2/Si standard sample is used to calibrate the intensity scale.

The experimental intensities for the samples are compared in Fig. 1 to those calculated by the electron scattering model and found to be in close agreement. For all the samples, the intensity begins to increase and then decreases

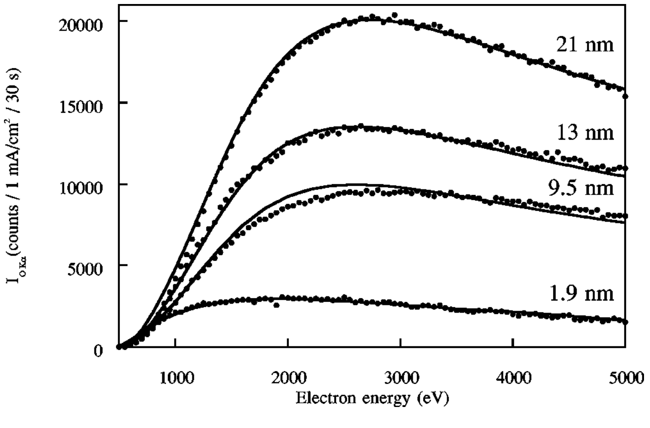

FIG. 1. O K_α intensity as a function of the electron energy for the various SiO_2/Si samples. The indicated SiO_2 thicknesses are those deduced from the ellipsometry measurements. Dots: EXES experiments normalized for 1 mA/cm^2 and 30 s; line: simulations performed with the semi-empirical electron scattering model taking into account the charging effect.

for E_0 greater than 2–3 keV. Indeed, as soon as the electrons reach the surface the characteristic x-ray line is emitted. However, the intensity decreases because the ionization cross section decreases, and at high energies the film thickness is smaller than the analyzed one. The intensity threshold takes place at the energy threshold of the O K_α emission (i.e., for an electron energy equal to the O 1s binding energy). This shows that the potential at the surface of the sample is zero and that the Cazaux's model can be applied.

The results deduced from the intensity modeling are reported in Table I and compared to those obtained by ellipsometry and reflectometry. The agreement is remarkable between the three techniques, and the uncertainty on the thickness determination by EXES is lower than 5%. The largest scatter is obtained with the 9.5 nm sample, which presents a discrepancy between the ellipsometry and reflectometry measurements. Note that the largest deviation between the excitation curves and the electron scattering model is also observed for this sample (Fig. 1). This could be due to the fact that the thickness of this film is not homogeneous.

We have shown in this letter that, for the thickness analysis of thin films, the EXES in association with a semiempirical electron scattering model provides results in excellent agreement with spectroscopic ellipsometry and x-ray reflectometry measurements. In the present case of thin insulating SiO_2 films, the small charging effect occuring upon the electron irradiation is taken into account by introducing a retarding potential in the model. The benefit of the EXES technique compared to the classical electron probe microanalysis is to operate at low primary electron energy from the threshold energy of O K_α emission up to 5 keV and to use large analysis surface area, both of which considerably reduce the charging effects. The EXES in association with its model is a well-suited technique for an accurate, quantitative, and nondestructive analysis at high depth resolution of thin films with an uncertainty lower than 5% for the thickness determination.

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