

## NANOMETROLOGY

### ELECTRON PROBE MEASUREMENTS OF OXIDE FILM THICKNESS ON SILICON SURFACES

V. P. Gavrilenko,<sup>1</sup> A. Yu. Kuzin,<sup>1</sup> V. B. Mityukhlyayev,<sup>1</sup>  
M. A. Stepovich,<sup>2</sup> P. A. Todua,<sup>1</sup> and M. N. Filippov<sup>1,3</sup>

*An electron probe method for measuring the thickness of oxide films on silicon surfaces is proposed. The measurement range, lateral resolution, and measurement errors are estimated.*

**Keywords:** *oxide film, thickness, electron probe analysis.*

Measurements of the thickness of oxide films on silicon surfaces are important in nanotechnologies, electronics, and metrology. The range with a lower bound corresponding to the 2–6 nm thickness of a natural oxide film and an upper bound of 30–50 nm is currently of greatest interest. There are only a few methods for measurement in this range. The best developed optical method, ellipsometry, is limited: it requires knowledge of the optical constants of the layers and its lateral resolution is about 10  $\mu\text{m}$  [1]. This makes it difficult to measure the thickness of oxide nanofilms on individual elements of stepped relief structures, especially on structures used for calibration of electron microscopes. We have proposed [2] a method for measurements on surfaces with these structure by means of a transmission microscope. It has unique metrological characteristics (the lower bound of the measurement range is tenths of a nanometer), but it is destructive, since it requires preparation of a thin transverse section of the structure being studied. For this reason, there is considerable interest in creating a nondestructive method for measuring the thickness of oxide films on silicon surfaces.

Recent improvements in the energy dispersion x-ray spectrometers (EDS) used in electron probe microanalysis (lower sensitivity limits, correct operation with high loads, etc.) mean that the dependence of the characteristic x-ray emission from oxygen on the thickness of an oxide film can be used for these measurements.

In this paper, we propose an electron-probe method for measuring the thickness of oxide films that is compatible with scanning electron microscopy (SEM). A linear section of the dependence of the intensity of the oxygen  $K\alpha$  line (0.525 keV) on the oxide film thickness is used for the measurements. The electron probe of the SEM is positioned on the part of the structure chosen for the measurements (which must be strictly perpendicular to the electron probe) and the x-ray spectrum is recorded. It is best to use a probe electron energy of 3–10 keV, since at higher energies the conditions for excitation of the signal are not optimal and the lateral resolution is reduced. A probe current ranging from 0.1 to several nanoamperes is chosen from the load conditions for the EDS. Similar conditions can be set in most modern SEM equipped with EDS.

x-Ray emission of oxygen in a thin film on a bulk substrate is excited by the primary electron beam and the flux of backscattered electrons passing through the film. Here most of the backscattered electrons are produced in the silicon substrate. In addition, a significant second-order effect can occur: the energies of the characteristic x-ray photons of silicon (1.740 keV

<sup>1</sup> Research Center for the Study of the Properties of Surfaces and Vacuum (NITsPV), Moscow, Russia; e-mail: fgupnicpv@mail.ru.

<sup>2</sup> Kaluga State University, Kaluga, Russia; e-mail: m.stepovich@mail.ru.

<sup>3</sup> Institute of General and Inorganic Chemistry, Russian Academy of Sciences (IONKh RAN), Moscow, Russia; e-mail: fil@igic.ras.ru.

for the  $K\alpha_{1,2}$  line of silicon and 1.829 keV for the  $K\beta$  line of silicon) are sufficient to excite the  $K$ -series of oxygen (the absorption edge is at 0.532 keV) and fluorescence. The intensity of the characteristic oxygen emission can also depend on the variation in the energy of the electrons as they are slowed down in the film and on the absorption of that radiation by the material as it propagates from its source region to the surface in the direction of the spectrometer. In most cases, it is sufficient to estimate an upper bound for the film thickness. For our estimates, here we shall assume that the oxide film is silicon dioxide.

The contribution of bremsstrahlung can be neglected when evaluating the contribution of fluorescence of the oxide owing to radiation from the substrate. It is sufficient to estimate the contribution from the most intense  $K\alpha_{1,2}$  line of silicon. For this, we can modify the condition [3] that there are no matrix effects when analyzing the films. The influence of oxygen fluorescence excited by the characteristic emission of silicon can be neglected for oxide films with thicknesses up to  $t_1$  given by

$$t_1 = 0.1 \left( \mu_{\text{SiO}_2}^{\text{O}} \rho_{\text{SiO}_2} \right)^{-1}, \quad (1)$$

where  $\mu_{\text{SiO}_2}^{\text{O}}$  is the mass attenuation coefficient for the characteristic oxygen  $K\alpha$  line emission in an  $\text{SiO}_2$  film, and  $\rho_{\text{SiO}_2}$  is the density of the  $\text{SiO}_2$  film.

The mass coefficients  $\mu_{\text{SiO}_2}^{\text{Si}}$  and  $\mu_{\text{SiO}_2}^{\text{O}}$  for attenuation of the  $K\alpha_{1,2}$  silicon line and the  $K\alpha$  oxygen line, respectively, in  $\text{SiO}_2$  are given by

$$\mu_{\text{SiO}_2}^{\text{Si}} = \mu_{\text{Si}}^{\text{Si}} C_{\text{Si}} + \mu_{\text{O}}^{\text{Si}} C_{\text{O}}; \quad (2)$$

$$\mu_{\text{SiO}_2}^{\text{O}} = \mu_{\text{Si}}^{\text{O}} C_{\text{Si}} + \mu_{\text{O}}^{\text{O}} C_{\text{O}}, \quad (3)$$

where  $\mu_{\text{Si}}^{\text{Si}}$ ,  $\mu_{\text{O}}^{\text{Si}}$  are the mass attenuation coefficients of the  $K\alpha_{1,2}$  silicon line in silicon and oxygen, respectively;  $\mu_{\text{Si}}^{\text{O}}$ ,  $\mu_{\text{O}}^{\text{O}}$  are the mass attenuation coefficients of the  $K\alpha$  oxygen line in silicon and oxygen, respectively; and  $C_{\text{Si}}$ ,  $C_{\text{O}}$  are the mass fractions of silicon and oxygen in the oxide film.

For  $\text{SiO}_2$ ,  $C_{\text{Si}} = 0.4676$ ,  $C_{\text{O}} = 0.5324$  and the mass attenuation coefficients  $\mu_{\text{Si}}^{\text{Si}} = 3630 \text{ cm}^2/\text{g}$  and  $\mu_{\text{O}}^{\text{Si}} = 989 \text{ cm}^2/\text{g}$  [4]. The density of the oxide film is  $\rho_{\text{SiO}_2} = 2.2 \text{ g/cm}^3$ . Substituting these values in Eqs. (1) and (2), we obtain an estimate of  $t_1 \approx 200 \text{ nm}$  for the upper bound on the oxide film thickness below which fluorescence excitation can be neglected.

Absorption of the characteristic emission from oxygen by the material in the film can be neglected up to oxide film thicknesses of  $t_2$  given by

$$t_2 = 0.1 \sin \Psi \left( \mu_{\text{SiO}_2}^{\text{O}} \rho_{\text{SiO}_2} \right)^{-1}, \quad (4)$$

where  $\Psi$  is the angle between the plane of the sample and the direction to the spectrometer.

For  $\Psi = 30^\circ$  and the value of  $\mu_{\text{SiO}_2}^{\text{O}} = 4496 \text{ cm}^2/\text{g}$  calculated using Eq. (3) for  $\mu_{\text{O}}^{\text{O}} = 980 \text{ cm}^2/\text{g}$  and  $\mu_{\text{Si}}^{\text{O}} = 8500 \text{ cm}^2/\text{g}$  [4], we find  $t_2 = 100 \text{ nm}$ . The change in the energy of the primary electrons in the oxide film can be estimated using the Bethe formula [5]:

$$\Delta E = 7.85 \cdot 10^{-3} (\bar{Z} / (ME)) \ln(1.166 E / J) t, \quad (5)$$

where  $\Delta E$  is the average energy loss in the film;  $\bar{Z}$  is the average atomic number of the oxide film;  $M$  is the relative molecular mass of the oxide film;  $E$  is the electron energy;  $J = 13.5 \cdot 10^{-3} \bar{Z}$  is the average ionization energy; and  $t$  is the thickness of the oxide film.

The average atomic number of the film is given by

$$\bar{Z} = Z_{\text{Si}} c_{\text{Si}} + Z_{\text{O}} c_{\text{O}}, \quad (6)$$

where  $Z_{\text{Si}} = 16$  and  $Z_{\text{O}} = 8$  are the atomic numbers of silicon and oxygen, respectively, and  $c_{\text{Si}}$  and  $c_{\text{O}}$  are the atomic fractions of silicon and oxygen, respectively, in the oxide film.

For an energy  $E = 5 \text{ keV}$  and an  $\text{SiO}_2$  film with a thickness of  $t = 100 \text{ nm}$ , Eqs. (5) and (6) yield  $\Delta E = 0.1 \text{ keV}$ .

Thus, secondary fluorescence, internal absorption, and variations in the probe electron energy can be neglected. In this case, the intensity of the characteristic oxygen emission of the oxide film is determined by two main processes: the generation

of radiation during passage of the primary radiation through the film and the generation of x-ray emission by the flux of back-scattered electrons from the substrate (we neglect the contribution of electrons backscattered in the film).

The variation in the intensity of the oxygen emission in the oxide film can be determined in the following way: we use a diffusive model for the interaction of an electron beam with a solid [6]. Numerous experimental confirmations of the equations of Ref. 6 for the mean free path of electrons in solids and estimates of the sizes of the different interaction regions indicate a spread of no more than 5–10% [7]. We assume that the probe electrons initially move deep into the sample without changing direction up to a certain depth corresponding to the maximum energy loss by the electrons. After that point, the average velocity vector of the electrons changes from the original direction and the electrons subsequently move in all directions with equal probabilities, i.e., this point can be regarded as a point source of electrons inside the sample. We consider the variation in the electron energy in terms of a continuous loss model [6], according to which backscattered electrons emerge from the sample surface in a region bounded by a circle with its center at the point where the electron beam is incident on the sample and a radius of

$$r_B = 2R\gamma/(1 + \gamma), \quad (7)$$

where  $R$  is the mean free path of the electrons in the sample,  $\gamma = 0.187Z^{2/3}$ , and  $Z$  is the atomic number of the sample material.

We calculate the electron mean free path  $R$  in a way similar to that proposed in [6]:

$$R = 0.0276AE_0^{5/3} / (\rho Z^{8/9}), \quad (8)$$

where  $E_0$  is the energy of the probe electrons,  $A$  is the relative atomic mass, and  $\rho$  is the density of the material.

In this model for the interactions of an electron probe, two fluxes of electrons irradiate an oxide film on the surface: the focussed electron probe of the instrument (electrons moving from the film surface toward the substrate) and a counter flow of backscattered electrons from the substrate. Here the region in which the oxygen signal is excited by the probe electrons is determined by the effective beam diameter (a few nanometers), while the backscattered electrons irradiate a circular spot of radius  $r_B$ . The size  $2r_B$  of the region bombarded by the backscattered electrons determines the lateral resolution of this method for measuring the thickness of oxide films. This size can be estimated by substituting the initial electron energy in Eqs. (7) and (8) while neglecting the energy loss  $\Delta E$  in the film. For a silicon substrate ( $Z = 16$ ;  $A = 28.1$  g/mole,  $\rho = 2.33$  g/cm<sup>3</sup>) and a probe electron energy  $E_0 = 5$  keV, we then obtain  $R \approx 0.42$   $\mu\text{m}$  and  $r_B \approx 0.14$   $\mu\text{m}$ . The lateral spatial resolution of this technique is about 0.3  $\mu\text{m}$ .

The intensity of the oxygen x-ray emission excited in the oxide film by the electrons in the focussed probe can be written in the form:

$$I_1 = \frac{\Delta\Omega}{4\pi} k I_e C_0 \frac{\omega_K N_A}{M_f} \rho_f Q(E_0, E_K) t,$$

where  $\Delta\Omega$  is the collection angle for the EDS;  $k$  is a coefficient that determines the detection efficiency;  $I_e$  is the electron probe current;  $C_0$  is the mass fraction of oxygen in the oxide film;  $\omega_K$  is the fluorescence yield for the  $K$ -shell of oxygen;  $N_A$  is the Avogadro number;  $M_f$  is the relative molecular mass of the oxide film;  $\rho_f$  is the density of the oxide film;  $E_K$  is the ionization energy of the  $K$ -shell of oxygen; and  $Q(E_0, E_K)$  is the electron-impact ionization cross section of the  $K$ -shell.

To estimate the x-ray signal produced by backscattered electrons, it must be noted that their energy is considerably below that of the primary probe electrons. The average energy of the backscattered electrons is given by the empirical formula [8]

$$\bar{E} = 1.09E_0(1 - Z^{-0.3}).$$

The angular distribution of the backscattered electrons is described, with acceptable accuracy, by the Lambert (cosine) law. After integrating over all exit angles, for the intensity  $I_2$  of the oxygen emission owing to backscattered electrons we obtain:

$$I_2 = \frac{\Delta\Omega}{4\pi} 2\eta_0 k I_e C_0 \frac{\omega_K N_A}{M_f} \rho_f Q(\bar{E}, E_K) t,$$

where  $\eta_0$  is an integral coefficient for the backscattered electrons that is given by the empirical formula [9]

$$\eta_0 = -0.0254 + 0.016Z - 1.86 \cdot 10^{-4}Z^2 + 8.31 \cdot 10^{-7}Z^3.$$

As shown above, absorption of the radiation in the film, as well as the additional excitation of a signal by the characteristic emission from the substrate, can be neglected, and the oxygen emission intensity will be related to  $t$  in the following way:

$$I = \frac{\Delta\Omega}{4\pi} 2\eta_0 k I_e C_0 \frac{\omega_K N_A}{M_f} \rho_f [Q(E_0, E_K) + 2\eta_0 Q(\bar{E}, E_K)] t. \quad (9)$$

After normalization to the experimental geometry and the probe current, Eq. (9) can be used for measuring  $t$ , once the corresponding ionization cross section has been calculated. This can be done using a formula employed in electron-probe microanalysis [10]:

$$Q(E, E_K) = \frac{\pi e^4 z_K b_K}{(4\pi\epsilon_0)^2 E_K^2} \frac{\ln(E/E_K)}{E/E_K}, \quad (10)$$

where  $e$  is the electronic charge;  $z_K$  is the number of electrons in the  $K$ -shell;  $b_K = 0.35$ ; and  $E$  is the energy of a probe electron or the average energy of the backscattered electrons.

This formula makes it possible to measure  $t$ , but for  $t < 60$  nm the error is 20–60%, owing to the major simplifications in deriving Eq. (10). Nevertheless, in many cases this level of accuracy may be sufficient.

A significant improvement in the accuracy characteristics of this method can be achieved by using a comparison sample with the same structure and composition (oxide film on silicon). An experiment with a comparison sample consisting of an oxide film on silicon; the film thickness was found to be  $15.5 \pm 0.6$  nm on a transmission electron microscope along a specially prepared cut. Given Eqs. (1) and (4) for a sample with this structure, the expression for the x-ray emission intensity will be analogous to Eq. (9). Assuming that the density, molecular mass, and elemental composition of the film being studied and those of the comparison sample are the same, and that the experimental conditions (electron energy, probe current, position of the samples relative to the electron probe and EDS) are identical, Eq. (9) yields  $t = t_0 I/I_0$ , where  $t_0$  is the thickness of the oxide film in the comparison sample, and  $I$  and  $I_0$  are the intensities of the oxygen line from the oxide films in the test sample and comparison sample, respectively.

The method was tested by growing an oxide film by plasma processing on a silicon surface upon which a relief structure was initially formed.  $t$  for the relief surface could not be determined ellipsometrically.  $t$  was measured on the surface of the relief structure (prior to plasma processing) and for three samples subjected to processing for different times with a JSM-6460 LV SEM with an EDS. It was found that the unprocessed sample had  $t = 1.3$  nm, and the processed samples had thicknesses of 2.5, 3.5, and 4.6 nm. Then slices of these structures were prepared by the method of [2] and the thickness  $t$  was determined in a transmission electron microscope. The discrepancies in this range did not exceed 20%.

The method for measuring the thickness of oxide films described here has a number of advantages; in particular, it has high lateral resolution (tenths of a  $\mu\text{m}$  to a few  $\mu\text{m}$ ) and is nondestructive. The measurement error for thicknesses in the range of a few nanometers is 15–25%.

This work was supported by the Russian Science Foundation (Agreement No. 14-19-01652 of June 27, 2014).

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