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Experimental Determination of the Energy Dependence of Electron Inelastic Mean Free Path in Silicon Oxide and Silicon Nitride

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Abstract—The energy dependence of the electron inelastic mean free path, λ(*E*), in silicon oxide and silicon nitride is experimentally determined via Auger electron spectroscopy according to Auger signal attenuation with varying film thickness. Silicon-oxide- and silicon-nitride films are formed on different metal substrates by means of plasma-enhanced chemical vapor deposition. Analysis of the results and their comparison with theoretical data indicate that, in the chosen material, variations in the electron mean free path versus their energy are estimated more reliably by means of experiments than through the use of universal theoretical curves. It appears that the results obtained in this work can help in the more accurate determination of the width and location of interfaces in multilayer structures.

Keywords: electron inelastic mean free path, Auger electron spectroscopy

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INTRODUCTION

The determination of the energy dependence of the electron inelastic mean free path (IMFP) λ(*E*) (i.e., the average distance traveled by an electron before inelastic scattering) [1] is important for quantitative chemical analysis of the surface and nearsurface regions of solids by Auger electron spectroscopy (AES) [2, 3] and X-ray photoelectron spectroscopy (XPS) [4], especially for the study of element's distribution in nanolayers and interfaces. Since the electron escape depth depends on the IMFP, the value of λ specifies the analyzable volume in the aforementioned methods. In addition to practical necessity, the experimental determination of quantity λ and its dependence on the electron energy is of independent fundamental interest from the viewpoint of the interaction between electrons and a substance and because the correctness of theoretical models describing the given interaction can be verified.

The materials under investigation were silicon oxide and silicon nitride obtained by plasma-enhanced chemical vapor deposition (PECVD), which are widely used in modern electronics.

The purpose of this work is the exerimental determination of the dependence λ(*E*) in silicon oxide and silicon nitride by analyzing the attenuation of the Auger peaks.

The inelastic IMFP of electrons [5], i.e., the average distance that an electron travels between two inelastic scattering events, characterizes the depth resolution in AES and XPS. However, the Auger electron or photoelectron escape depth is directly affected by the electron trajectory projection on the chosen direction, namely, the so-called attenuation length *L*. Terms λ and *L* are often employed as synonyms, but each has its own meaning [6]. When quantity λ is calculated, the electron trajectory changes caused by elastic interactions are not taken into account. At the same time, their influence on *L* is substantial. Hence, the quantities *L* of different materials are experimentally established with the highest accuracy, and theoretical calculations must be carried out with elastic scattering taken into account. In many respects, the difference between *L* and λ depends on the experiment under consideration [7, 8]. As was revealed in [4], expression $L \approx \lambda\cos\alpha$, where α is the analyzer's collection angle, is valid for AES and XPS.

DESCRIPTION OF THE SAMPLES

Value of *L* is the most important parameter in AES and XPS depth profiling. Since the1960s, many researchers have attempted to determine this value. Investigations have been carried out in two directions: theoretical calculation of the energy dependence of *L* and its experimental determination based on AES and XPS data. As opposed to theoretical works, experimental data were not numerous and had a large disperion, which was most likely related to an inhomogeneous film thickness, a large roughness, possible impurity segregation at the film–substrate interface, and so forth. The small number of experimental values

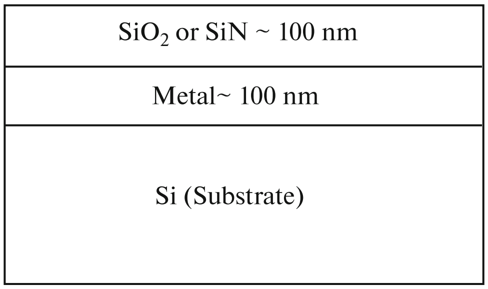

Fig. 1. Structure of the samples.

of L can be explained by difficulties in samples preparation.

Experiment was performed using 16 fabricated samples: eight with SiO$_2$ and eight with SiN. A schematic representation of the samples is depicted in Fig. 1. Metals films were obtained by the magnetron deposition method with the help of a TM Magna 150 system. Ti, Al, NiCr, Ni, Ta, Nb, Mo and FeNi films were employed. The metal films were cleaned by means of a Corial D-250 system intended for the PECVD of insulators to remove carbon-contaminated layers. Afterward, the films were oxidized to a depth of ~50 nm in nitrous oxide. Thus, a sharp interface between the insulators and metal oxide, which has a constant composition in the layer ~50 nm thick, was formed. In this case, the analyzed Auger peak intensity was changed due to variations in the insulator-layer thickness instead of the concentration at the interface. With the help of the system indicated above, silicon-nitride- and silicon-oxide layers were deposited in the same cycle without breaking vacuum conditions. The SiO$_2$ (SiN) precursors were SiH$_4$ and N$_2$O (SiH$_4$ and NH$_3$).

EXPERIMENTAL

The prepared insulator layers were investigated by means of AES using a Physical Electronics PHI-670xi Auger spectrometer with a Schottky field-emission hot cathode and a cylindrical mirror analyzer. During spectrum recording, the constant relative energy resolution was 0.5%. The accelerating voltage of the primary electron beam was 5 kV, and the primary-current density was no more than 10 μA/cm^2. Under such conditions of analysis, the spectrum recording process was not accompanied by changes in the structure of the insulator and local diffusion effects were not detected in the region irradiated with the primary electron beam. Spectra were recorded in the integrated form. Subsequently, differentiation with respect to five points and smoothing over five points were carried out with the help of the Savitzky-Golay algorithm [9]. The peak amplitude of the differential spectrum was taken as the Auger signal intensity.

After the samples were fabricated, the stoichiometry of the insulator film was determined. Investigations were performed via AES by comparison with standard samples prepared from thermally oxidized films. It was revealed that the stoichiometry of the samples is similar to that stated. In the oxide film, the ratio between the Si and O atomic concentrations was 0.499 ± 0.012. In the nitride film, the ratio between the Si and N atomic concentrations was 1.033 ± 0.108.

Each element has a strictly defined number of Auger peaks corresponding to the different allowed Auger transitions of electrons (*KLL*, *LMM*, *MNN*, and so on) in the atom. The Auger electrons energy is in the range of 30–3200 eV. Hence, the experiment was carried out with metals whose Auger peak energies practically overlapped this range: Ti, Al, FeNi, Nb, NiCr, Ta, Mo and Ni. Each Auger electron energy is characterized by its own value of λ. The quantities λ were calculated according to the Auger peak intensity attenuation curve when the insulator layer thickness was decreased.

In the case where a thin layer of some material is deposited onto a substrate made of another material, the general formalism indicates that the AES or XPS signal intensity can be represented as

$$\begin{gathered} I_l = I_l^{\infty}\left[1-\exp\left(-x/\lambda_i^l\cos\alpha\right)\right], \\ I_s = I_s^0\exp\left(-x/\lambda_i^s\cos\alpha\right), \end{gathered} \tag{1}$$

where I_l is the signal intensity of the upper layer (film), I_s is the signal intensity of the lower layer (substrate), x is the traversed layer thickness, I_s^0 is the substrate's signal intensity in the absence of an insulator film, I_l^{∞} is the signal from an infinitely thick insulator film, and α is the analyzer's collection angle. In the case of a cylindrical mirror analyzer, $\alpha \approx 42° \pm 6°$.

When the insulator film was sputtered by a 2 keV Ar$^+$ ion beam incident at an angle of 10° to the surface, the Auger-peak intensities of the given structure were recorded at equal time intervals with the help of the PHI-670 xi spectrometer. Sputtering was implemented until the insulator-layer signals disappeared. The dependences between the intensity of Auger signals corresponding to different peaks and the sputtering time were obtained. Afterward, an Alpha-Step D-120 contact profilometer was used to measure the ion-etching crater depth, determine the sputtering rate, and calculate the value of x, i.e., the difference between the thicknesses of two successively created SiN or SiO$_2$ layers:

$$\Delta x = \Delta t D_{\mathrm{SUM}}/T_{\mathrm{SUM}}, \tag{2}$$

where D_{SUM} is the ion-etching crater depth measured by means of the profilometer and T_{SUM} is the total etching time.

The roughnesses *Ra* of the initial surface and the ion-etching crater bottom were simultaneously monitored. This quantity remained practically unchanged and was 0.25–0.35 nm.

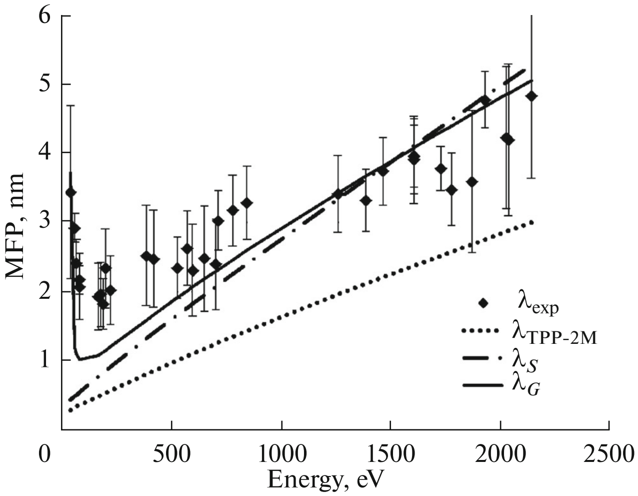

Fig. 2. Dependences between the MFP of electrons and their energy in SiO_2.

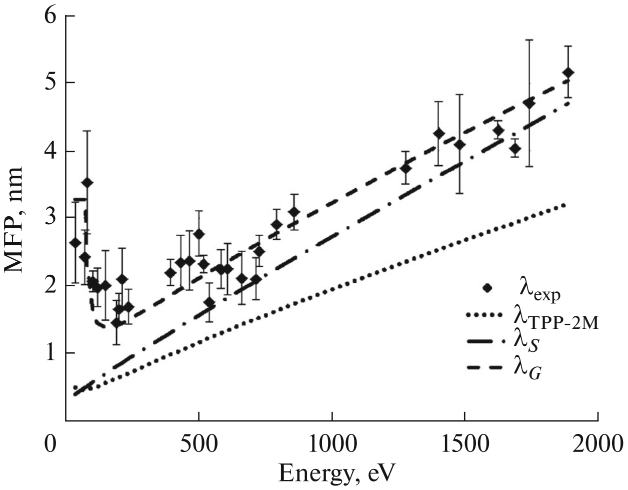

Fig. 3. Dependences between the MFP of electrons and their energy in SiN.

Subsequently, the quantity $L = \lambda\cos\alpha$ was calculated for each Auger peak energy. In the case where the Auger peak corresponds to electrons emitted from a metal, the ratio between the intensities of two successive layers takes the form

$$I_1/I_2 = \exp(-x_1/L)/\exp(-x_2/L). \tag{3}$$

Therefore, λ is expressed as

$$\lambda = \Delta x/\ln(I_1/I_2)\cos\alpha. \tag{4}$$

When the Auger peak corresponds to electrons emitted from the insulator itself, we obtain

$$I_1/I_2 = \frac{I_0(1-\exp(-x_1/L))}{I_0(1-\exp(-x_2/L))}. \tag{5}$$

Thus,

$$\lambda = \frac{\Delta x}{\ln((I_0 - I_1)/(I_0 - I_2))\cos\alpha}, \tag{6}$$

where I_0 is the signal intensity of a thick insulator layer.

For each sample and each peak under study, we calculated the quantity λ. Two independent sets of dependences λ(*E*) were found. The average value of λ inherent to each energy was determined via statistical processing. Moreover, experimental data were approximated by the equation

$$\lambda = aE^b + cE^d, \tag{7}$$

which is analogous to that proposed by Seah et al. [5] who approximated a large collection of experimental data obtained by different authors.

The experimentally revealed energy dependence of the IMFP in SiO_2 has the form

$$\lambda = 0.1531E^{0.4352} + 202.4E^{-1.5}. \tag{8}$$

In this case, the reliability (*r*) of the approximation is 0.9496.

The energy dependence of the IMFP in SiN, which was experimentally obtained with the reliability (*r*) of the approximation of 0.9168, is expressed as

$$\lambda = 7.78E^{-0.2946} + 9.673\times10^{-4}E^{1.11}. \tag{9}$$

COMPARISON BETWEEN THE EXPERIMENTAL RESULTS AND MAIN THEORETICAL DEPENDENCES

The experimental results were compared with the calculations of other authors. The models of comparison were formulas suggested by Seah [7, 10], Tanuma, Powell, and Penn (TPP-2M formula) [8, 11, 12], and Gries [6, 13]. For SiO_2 and SiN, the results of comparison are presented in Figs. 2 and 3.

In accordance with the model proposed by Seah (National Physical Laboratory, Great Britain) [7, 10],

$$\lambda_S = (0.65 + 0.007E^{0.93})/Z^{0.38}\ \text{(nm)}, \tag{10}$$

$$Z = (\mathrm{g}Z_\mathrm{G} + \mathrm{h}Z_\mathrm{H})/(\mathrm{g} + \mathrm{h}), \tag{11}$$

where *Z* is the average atomic number of G_gH_h compounds. This formula makes it possible to predict the IMFP in a material with known atomic number and stoichiometry. However, the given formula can be applied to the description of electrons with energies of greater than 100 eV only. Moreover, this model involves the free electron approximation.

In accordance with the model suggested by Tanuma, Powell, and Penn (National Institute of Standards and Technology, USA) [8, 11, 12],

$$\lambda_{\text{TPP-2M}} = E/E_p^2(\beta\ln(\gamma E) - C/E + D/E^2)\ (\text{Å}), \tag{12}$$

$$\beta = -0.10 + 0.944/(E_p^2 + E_g^2)^{0.5} + 0.069\rho^{0.1}, \quad (13)$$

$$\gamma = 0.191\rho^{-0.5}, \quad (14)$$

$$C = 1.97 - 0.91U, \quad (15)$$

$$D = 53.4 - 20.8U, \quad (16)$$

$$U = N_{\mathrm{v}}\rho/M = E_p^2/829.4, \quad (17)$$

where $E_p^2 = 28.8(N_v\rho/M)^{1/2}$ (eV), $N_v\rho$ is the number of valence electrons both in an atom (simple elements) or in a molecule (chemical compounds), ρ is the density (g/cm^3), M is the relative atomic or molecular mass, and E_g is the band-gap width (eV). This formula enables us to predict the IMFP in inorganic compounds where the electron energies are 100–2000 eV. This model also incorporates the free electron approximation.

In accordance with the model proposed by Gries (Research Center of the Deutsche Telekom, Germany) [6, 13],

$$\lambda_G = \frac{k_1(V_a/Z^*)E}{\log E - k_2}, \quad (18)$$

$$Z^* = \frac{p\sqrt{z_{\mathrm{B}}} + q\sqrt{z_{\mathrm{A}}} + \ldots + r\sqrt{z_{\mathrm{C}}}}{p + q + \ldots + r}, \quad (19)$$

$$V_a = \frac{pM_{\mathrm{A}} + qM_{\mathrm{B}} + \ldots + rM_{\mathrm{C}}}{\rho(p + q + \ldots + r)}, \quad (20)$$

where V_a is the atomic volume; k_1 and k_2 are the approximation coefficients; Z^* is a real number, which can be considered the nominal "effective" number of interaction-prone electrons in A_pB_q compounds; and ρ is the density (g/cm^3). The above equations are based on the orbital interaction model.

The first two curves are valid and applicable at electron energies of more than 150 eV. The third curve is semiempirical and comprises not only material parameters but also fitting coefficients used in the approximation and, hence, describes experimental data to a better extent.

CONCLUSIONS

In this work, samples of films made of two insulators (silicon oxide and silicon nitride) are investigated by Auger-electron spectroscopy. The experimental dependences of the inelastic mean free path thereof are obtained. The IMFP values are determined by analyzing the Auger peak intensity attenuation in different elements. In performing the experiments, the main problem lies in creating an abrupt interface between an insulator deposited onto a metal film and the film itself. Hence, metals are preliminarily oxidized to obtain oxide layers with a constant composition and a thickness of ~50 nm, i.e., the abrupt insulator–metal interface is attained. The analyzed Auger peak intensity is changed due to variations in the insulator-layer thickness rather than in the concentration at the interface.

Two independent sets of values of $\lambda(E)$ are obtained, and the average value of λ for each energy is determined by means of statistical processing. Analysis of the results and their comparison with published theoretical data indicates that, in a particular material, experimental determination of the IMFP of electrons versus their energy provides more accurate values than universal theoretical curves.

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