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Applying the In Situ X-Ray Reflectometry Method to Define the Nanodimensional Silicon Film Parameters

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Abstract—The monitoring methods for measuring the film structure parameters in formation process, namely, the in situ methods, are currently of special significance. Their application provides obtaining the films with the given characteristics, which results in a fast correction of the technological modes. The possibilities of the in situ method of the X-ray reflectometry for defining the parameters of the nanodimensional films during their formation are discussed. The results are given of testing the magnetron deposition of the silicon films and other materials on the silicon substrate.

Keywords: silicon, magnetron deposition, X-ray reflectometry

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INTRODUCTION

Today the production of the optics and microelectronics items requires forming one-layer and multilayer compositions with different functions on dielectric, semiconductor, and metal substrates. The examples of such structures can be optic interference claddings, mirrors of a soft X-ray range, and semiconductor superlattices. The peculiarity of modern electronics lies in the use of progressively thinner layers and the transition from the microdimensional to the nanodimensional films. The application of such claddings makes increased demands on the quality of the substrate cladding, the state of the borders between the layers, and the homogeneity of separate layers. The surface state can be experimentally estimated by various physical (optic and probe) methods, each of which has its own advantages and application area. The monitoring methods allowing one to measure the film structure parameters directly during their formation, namely, the in situ methods, have gained great significance. They provide obtaining films with the given parameters, allowing one to correct the technological modes quickly.

In the past ten years, many investigations on the growth and ion etching of thin films using different methods were carried out. However, the studied process breaks in most of them. The samples are tested in air. Clearly, such an approach has some disadvantages.

(1) Oxidation of the surface often leads to the increased roughness in comparison with the one formed immediately after deposition.

(2) Interaction between the surface and air leads to a change in the near-surface layer, including the formation of the oxide and adhesion layers.

(3) Artifacts can appear upon investigating the samples (e.g., films that are different in thickness films coated on identical substrates).

(4) Research work without a camera after termination of the technological process (ex situ) often does not provide an exact determination of the temporary evolution of the sample parameters with respect to the technological parameters, e.g., annealing time.

Below we give the studied possibilities of the in situ method of the X-ray reflectometry for defining nanodimensional films in real time.

EXPERIMENTAL

In the simple variant, the in situ X-ray reflectometry can be implemented based on the analysis of the temporary dependence between the intensity of the specularly reflected X-ray beam from the sample, which is recorded at the fixed sliding angle θ_0. As a result of changing the phase difference in the waves reflected by the growing film and substrate surfaces, the interference image represents the oscillations of the X-ray radiation intensity [1]. To implement the method, a vacuum technological complex, including a vacuum camera, deposition node, and measuring X-ray reflectory system, was generated.

In practice, the rate at ehich the films are formed generally lies in the range from tenths of a fraction to units of nanometers per second. This constrains the data processing time and requires simplifying the calculation algorithm. In the general case, the coefficient of the reflection from the system, the film–substrate is described by recurrent expressions [3]. Recording the time dependence of the reflection coefficient R of the

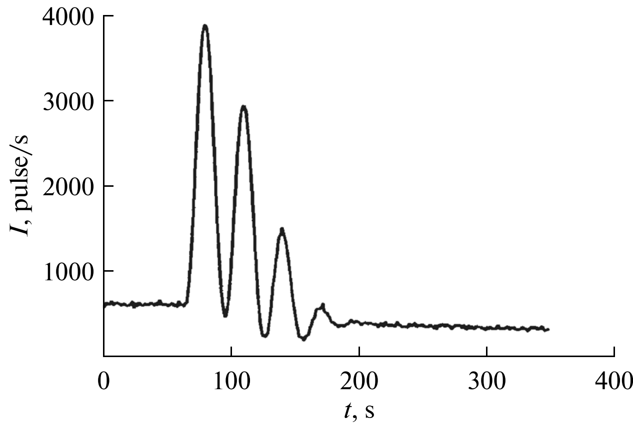

Fig. 1. The relationship between the X-ray beam reflection coefficient and the titan film deposition time. The radiation is CuK_α, the sliding angle is 1°.

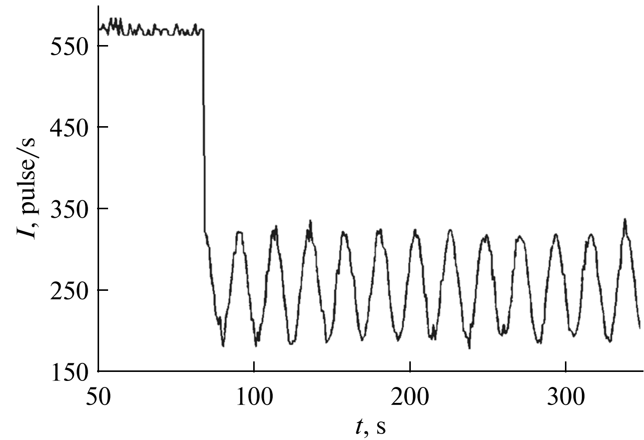

Fig. 2. The relationship between the X-ray beam reflection coefficient and the silicon film deposition time on the silicon substrate. The radiation is CuK_α, the sliding angle is 1°.

X-ray beams at the sliding angles exceeding the value of the critical angle of the full external reflection allows one to use the kinematic approximation, within which the formulae of the calculation of the growing film parameters can be simplified. In extremums, the expression for the specular reflection coefficient is

$$R = \frac{1}{16\sin^4\theta_0}\left[\left(\delta_2{}^2D^2 + (\delta_2 - \delta_1)^2 \pm 2\delta_2 D(\delta_1 - \delta_2)\right)\right],$$

where the sign ± corresponds to the minimal and maximal reflection coefficients $R_{\min}$ and $R_{\max,}$ with respect to the sign of $(\delta_1 - \delta_2)$; δ_1 and δ_2 are the decrements of the refraction coefficient of the X-ray beams for the substrate and the film, respectively; D is the multiplier, taking into account the change in the roughness of the film–vacuum border σ_{32} relative to the substrate roughness σ_{21}. Here, the Debye–Valera factor can serve as the last one,

$$D = e^{-\frac{1}{2}Q^2(\sigma_{32}-\sigma_{21})^2},$$

where Q is the scattering vector.

The value of the refraction decrement is linked to the material density ρ by the following relationship [4]:

$$\delta = \frac{N_0 e^2}{2\pi mc^2}\lambda^2\rho\frac{z}{A},$$

where z is the sum of the discharges (atomic numbers); A is the sum of the atomic weights of all the elements; N_0 is the Avogadro number; e and m are the charge and the mass of the electron; c is the speed of light.

We assume that the refraction decrements and roughness of the growing film are the changing functions of its thickness, which can be taken as constant on the oscillation half-period. Then, the density and the mean square roughness of the film averaged over the oscillation half-period are determined from the relationship between the mean square reflection coefficient $\langle R\rangle$ and the film-substrate system and contrast range $K = \dfrac{R_{\max} - R_{\min}}{R_{\max} + R_{\min}}$.

DISCUSSION OF THE RESULTS

One of the advantages of the X-ray reflectometry in situ method is the possibility to obtain the information about the growing film parameters directly during the technological process in real time. A typical experimental relationship between the X-ray radiation reflection coefficient and the film deposition time at the fixed sliding angle is shown in Fig. 1. The titan film deposition started after 65 s of recording the time dependence of the reflection coefficient. The values of $R(t)$ up to this time correspond to the reflection from the silicon substrate. Since the density of the precipitated metal is higher that the substrate density, the first extremum on the oscillating curve is the maximum whose position is defined by the Wolf–Bragg formula, taking the X-ray beam refraction into account. In these conditions, it is formed on the titan film achieving a thickness of ~2.3 nm. At a constant growth rate, the next extremums are located on the experimental curve with the same periodicity. The deposition process stopped at 170 s. The film thickness reached the value of 15.3 nm. The extremum frequency changes with the growth rate. When the thickness of the film at deposition increases, the oscillation amplitude decays. This is due to the increasing absorption and roughness of the film surface. At small film thicknesses and radiation absorption, the attenuation of the amplitude is generally induced by the increased roughness in the film–vacuum border.

If the density of the precipitated material is lower than that of the substrate, the first extremum is the minimum [2]. Figure 2 shows the test results of the silicon deposition on the silicon substrate. The mean square roughness of the used substrates, which was

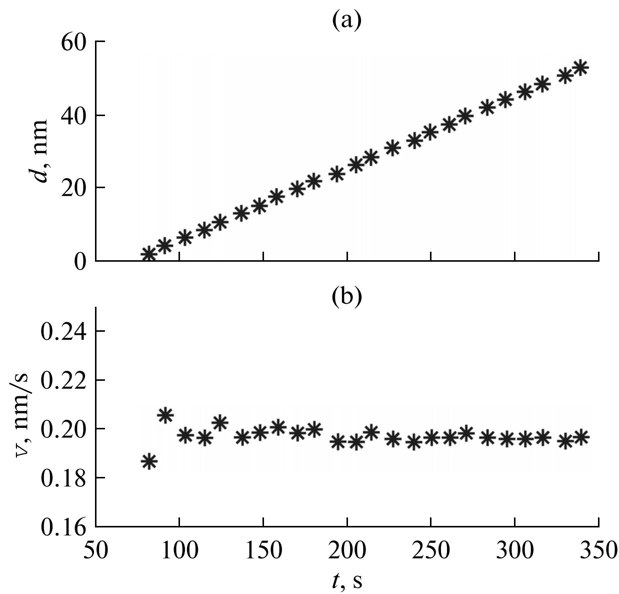

Fig. 3. The relationship between the width (a) and growt rate (b) and the silicon film deposition.

estimated by the independent probe microscopy and X-ray reflectometry methods, was 0.5 nm. This case is interesting, as there would be no oscillations on the experimental dependence due to the identical film and substrate densities at the epitaxial oscillation growth. However, the results show that the precipitated silicon film has the lower density compared to the substrate density at the magnetron deposition. The first extremum is the minimum. The general recorded intensity decreased.

Figure 3 depicts the dependences of the thickness and the film growth rate on the deposition time calculated by the experimental curve in Fig. 2. The presented relationship results in a constant growth rate at ~0.2 nm/s. The estimated values of the refraction decrement and the roughness of the film surface with respect to the deposition time are practically constant. The roughness of the precipitated silicon film surface was ~0.7 nm, and it changed slowly as the thickness increased to 55 nm. The refraction decrement was significantly lower than the volume of the material (7.65×10^{-6}). This proves that a silicon film ~2.1 g/cm^3 in density, which is less than the density of the volume of silicon (2.32 g/cm^3) is precipitated on the substrate surface. Probably, this is related to the porosity of the films formed by the magnetron deposition method. The generation of such a structure is mentioned in [5].

CONCLUSIONS

Based on the experimental investigation in real technological magnetron deposition, the possibilities of the X-ray reflectometry in situ method for determining the nanodimensional film parameters are the following:

—The method is nondestructive;

—It allows one to control the film thicknesses in the 1–100 nm range in the real time of formation;

—It allows estimating the density of the growing films and the roughness of their surfaces;

—There are no limitations on the type of studied materials in any film–substrate combinations;

—It does not influence the progress of the technological process, since the measuring system is outside the working camera.

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