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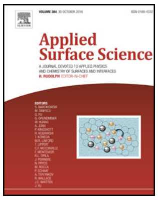

Full Length Article

Spectroellipsometric detection of silicon substrate damage caused by radiofrequency sputtering of niobium oxide

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ABSTRACT

Substrate surface damage induced by deposition of metal atoms by radiofrequency (rf) sputtering or ion beam sputtering onto single-crystalline silicon (c-Si) surface has been characterized earlier by electrical measurements. The question arises whether it is possible to characterize surface damage using spectroscopic ellipsometry (SE). In our experiments niobium oxide layers were deposited by rf sputtering on c-Si substrates in gas mixture of oxygen and argon. Multiple angle of incidence spectroscopic ellipsometry measurements were performed, a four-layer optical model (surface roughness layer, niobium oxide layer, native silicon oxide layer and ion implantation-amorphized silicon [i-a-Si] layer on a c-Si substrate) was created in order to evaluate the spectra. The evaluations yielded thicknesses of several nm for the i-a-Si layer. Better agreement could be achieved between the measured and the generated spectra by inserting a mixed layer (with components of c-Si and i-a-Si applying the effective medium approximation) between the silicon oxide layer and the c-Si substrate. High depth resolution Rutherford backscattering (RBS) measurements were performed to investigate the interface disorder between the deposited niobium oxide layer and the c-Si substrate. Atomic resolution cross-sectional transmission electron microscopy investigation was applied to visualize the details of the damaged subsurface region of the substrate.

1. Introduction

The technique of sputtering involves ejecting material from the target to the substrate such as a silicon wafer. Resputtering is re-emission of the deposited material during the deposition process by ion or atom bombardment. Sputtered atoms ejected from the target have a wide energy distribution, typically up to tens of eV. The sputtered ions and atoms can reach the substrate condensing after undergoing a random walk. High-energy neutrals sputtered from the target will still have enough energy reaching the substrate even after some collisions in the working gas to damage the surface of the crystalline substrate.

The radio frequency (rf) voltage may be applied directly to the cathode for metal sputtering or via capacitor to sputter insulators. The high frequency alternating potential may be used to neutralize the insulator surface periodically with plasma electrons, which must be switched in a period that is short compared with the time required by the positive ions to travel to the surface of target. Thus, both the amplitude and frequency of rf should be high to yield high rates. The insulator target may consist of different material: oxides, nitrides etc., from that not only atoms but molecules with considerable kinetic energy can be deposited. This is the reason why surface damage of the substrate can be significant as a result of rf sputtering deposition.

Substrate surface damage induced by deposition of metal atoms by rf sputtering or ion beam sputtering onto the single-crystalline silicon (c-Si) surface has been characterized earlier by I-V, C-V and deep-level transient spectroscopy measurements [1–3].

In our experiments niobium oxide layers were deposited by rf sputtering on c-Si substrates at room temperature in gas mixture of oxygen and argon. Optical properties of thin film structures can be derived from SE measurement, which is known to be a high-

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Table 1
Duration, pressure, oxygen flow, DC voltage (wall potential) of rf sputtering for different samples.

Sample	A495	A496	A497	A505	A504	A503	A247
Duration	100 s	150 s	300 s	30 min	30 min	30 min	120 min
Pressure [Pa]	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Oxygen flow[ml/min]	6	6	6	6	6	6	6
DC voltage [kV]	2.0	1.5	1.0	1.0	1.5	2.0	2.0

precision optical characterization technique [4–7]. Multiple angle of incidence (MAI) spectroscopic ellipsometry measurements were performed on the samples deposited by rf sputtering. Multilayer optical models (surface roughness layer, niobium oxide layer, a native silicon oxide layer and ion implantation-amorphized silicon (i-a-Si) layer on a c-Si substrate) were created in order to evaluate the spectra. The dielectric function of the niobium oxide was described by the Tauc–Lorentz dispersion relation or a Lorentz oscillator.

High depth resolution RBS measurements combined with channeling [8] were performed to investigate the interface disorder between the thin deposited niobium oxide layer and the c-Si substrate. Atomic resolution cross-sectional transmission electron microscopy (HRTEM) investigation was applied to visualize the details of the damaged subsurface region of the c-Si substrate. Calculations were performed using SRIM code (Stopping and Range of Ions in Matter) in order to interpret the details of the damage formation [9].

2. Experimental

Niobium oxide layers were deposited by rf sputtering on c-Si substrates at room temperature using a Leybold Z400 apparatus. Prior to the rf sputtering deposition the native oxide was removed from the silicon substrates using diluted HF.

The deposition was performed using niobium oxide powder target (Kurt J. Lesker Co.) in an Ar–O_2 atmosphere. During the sample preparation the pressure was adjusted to 0.3 Pa, the oxygen flow was chosen to be 6 ml/min, the DC sputtering voltage (wall potential) was selected from the range of 1.0–2.0 kV, and the duration of the sputtering was between 100 s and 120 min (the details are listed in Table 1).

For the ellipsometric characterization of the rf-deposited samples M-2000DI (Institute of Technical Physics and Materials Science, Centre for Energy Research, Budapest, Hungary) and M-2000F (Department of Optics and Quantum Electronics, University of Szeged, Hungary) rotating compensator spectroscopic ellipsometers manufactured by the J.A. Woollam Co., Inc. were used [10]. Multilayer optical models with the Tauc-Lorentz dispersion relation [11,12] or with a Lorentz oscillator and reference data from the literature [10,13] was applied for evaluation of ellipsometric spectra using the WVASE32 software [10].

RBS analysis was performed using the Hungarian Ion-beam Physics Platform 5 MV Van de Graaff accelerator in Budapest, at the Institute for Particle and Nuclear Physics, Wigner Research Centre for Physics of the Hungarian Academy of Sciences. The ion beam of 1000-keV $^4He^+$ was collimated with 2 sets of four-sector slits to the necessary dimensions of 0.5 mm × 0.5 mm. An ion current of typically 20 nA was measured by a transmission Faraday cap [14]. The dose of the measurements was 20 μC. The spectra taken on the samples were simulated with the same layer structure using the RBX program [15,16].

The microstructure of the films was investigated by HRTEM using a JEOL JM3010 transmission electron microscope operated at an acceleration voltage of 300 kV with an 0.17 nm point resolution. HRTEM images were taken in cross-sectional view.

Cross-sectional samples were prepared by creating a “sandwich” from two 1.8 mm × 0.5 mm pieces of the sample (film to film). This “sandwich” was mounted and glued (with an araldite-based glue) into the window of a Ti grid followed by mechanical thinning, polishing, and dimpling to a thickness of ca. 20 μm in the middle. Thinning to electron transparency was achieved by ion-beam milling [17] using a Technoorg Linda ion mill with 10-keV Ar^+ ions at an incidence angle of 5° with respect to the surface. In the final period of the milling process, the ion energy was decreased gradually to 0.3 keV (using a Technoorg-Linda Gentle Mill) to minimize ion-induced structural changes in the surface layers. Specimens prepared by small angle cleavage technique (SACT) [18] were investigated as well, in this case the possible disturbing effect of the ion-beam milling was avoided. The image taken on the cleaved piece was very similar to the one prepared by ion-beam milling.

3. Results and discussion

First, we evaluated SE spectra measured on the Nb-oxide sample deposited with 120 min duration and 2.0 kV wall potential. Various optical models (one-layer model, two-layer model, three-layer model and four-layer model) were created.

We consider the Mean Square Error (MSE) together with the measured and generated ellipsometric spectra in order to determine the quality of a model. Usually we create models with increasing complexity (with increasing number of sublayers) based on the information achieved from independent experiments for thin layers as high resolution RBS and cross sectional electron microscopy.

Table 2 shows the optical models together with the results yielded by the evaluations. The second, third, fourth and fifth columns represent the sublayers of the optical models. The c-Si substrate was not indicated in Table 2. The complex dielectric function of the Nb-oxide layer was modeled by the Tauc-Lorentz dispersion relation [11,12]. The optical model “A” contains only one layer, the Nb-oxide layer. The value of the Mean Square Error (MSE = 45.81) does not indicate a good correspondence between the measured and the generated spectra. After introducing a second layer, a surface roughness layer (model “B”), the evaluation yielded a considerably lower MSE value (36.87).

In the first three-layer model (model “C”) a silicon dioxide layer was inserted between the Nb-oxide layer and the c-Si substrate. A part of this silicon dioxide layer may originate from the native oxide formation during the time interval of placing the substrate into the processing chamber of the Leybold Z400 apparatus. Another part of this silicon dioxide layer may originate from a possible plasma oxidation prior to the start of the Nb-oxide layer formation. The evaluation performed using this three-layer model yielded MSE = 32.23. The second three-layer model (model “D”) contains an amorphous silicon layer between the Nb-oxide layer and the c-Si substrate.

For the description of the complex dielectric function of this amorphous silicon we selected the complex dielectric function of i-a-Si [13] because the damage was introduced by energetic ions and/or atoms. The evaluation has been performed in the wavelength range from 282 nm to 953 nm or from 1.3 eV to 4.4 eV because the complex dielectric function of ion-implantation amorphized silicon is available only in this range. It is important to note that the complex dielectric function of i-a-Si differs from that of amorphous silicon deposited by vacuum evaporation or by low-pressure chemical vapor deposition [13].

The evaluation performed with the second three-layer model (model “D”) gave a remarkable reduction of MSE, a value of 25.3 was obtained. The four-layer model “E” contains a silicon dioxide