EELS characterization of TiN grown by the DC sputtering technique

O. Contreras, A. Duarte-Moller. G.A. Hiratab, M. Avalos-Borja.

Abstract

Titanium nitride thin films were deposited on monocrystalline silicon (mc-Si) substrates by direct current reactive magnetron sputtering. Auger electron spectra (AES) of deposited films at different nitrogen partial pressures, show the typical N $KL_{23}L_{23}$ and Ti $L_3M_{23}M_{23}$ Auger transition overlapping. Also, changes in the Ti $L_3M_{23}M_{45}$ Auger transition peak are observed. X-ray diffraction and high resolution electron microscopy (HRTEM) of a golden color TiN/ mc-Si sample, reveal a preferential polycrystalline columnar growth in the k111l orientation. This sample was also analyzed by electron energy-loss spectroscopy (EELS). The N/Ti elemental ratio is slightly different to the value determined by AES. Atomic distribution around the N atoms is in agreement with that expected from the N atom in the fcc unit cell of TiN. This distribution was obtained via an extended energy-loss fine structure (EXELFS) analysis from EELS spectra.

Keywords*:* TiN; EELS; EXELFS; RDF

Introduction

Much attention has been directed toward the synthesis of carbide and nitride compounds. Titanium nitride thin films are a representative example of this kind of material. Titanium nitride has a unique combination of properties, such as high hardness, good chemical inertness, beautiful lustrous color and excellent wear resistance [1, 2]. Also, because it is a good diffusion barrier for metals and has a high

electrical conductivity, it can be applied in contact layers for solar cells and in silicon semiconductor devices [3,4].

Chemical vapor deposition (CVD), physical vapor deposition (PVD), ion implantation and, recently, pulsed laser deposition (PLD) are methods commonly used for deposition of TiN thin films. Several reports have been done on the influence of experimental parameters on TiN film properties [5,6] To carry out this study, it is important to have several techniques available for analysis. Auger electron and X-ray photoelectron spectroscopy are often used for TiN film quantification, while transmission electron microscopy and X-ray diffraction are the techniques commonly employed for micro- structural analysis. However, analysis techniques like electron energy-loss spectroscopy (EELS) are rarely employed for the characterization of thin films.

The characteristic energy losses of an electron beam penetrating through a film (transmission mode) can give important information on the nature of the solid. Within the energy loss mechanisms in an EELS spectrum, in the high-loss regime (above 50 eV), are the excitation and ionization of the atomic core levels. The atomic excitation and ionization edges represent a medium for element identification and quantification, particularly useful in cases where the spatial resolution of an electron microscope is required. Furthermore, an extended energy loss fine structure (EXELFS) analysis of atomic ionization edges gives information about the atomic near-neigh-bor distribution (RDF). Therefore, TEM with EELS in situ, represents a potential tool for quantitative and microstructural characterization of materials.

Titanium nitride thin films deposited by DC reactive magnetron sputtering at different nitrogen partial pressures, were analyzed by AES. One of them was chosen for analysis by X-ray diffraction, cross-sectional TEM and EELS.

Experimental

Titanium nitride coatings were grown in a physical vapor deposition system assisted by a direct current reactive magnetron sputtering technique. The vacuum chamber was evacuated with a mechanical pump and cryopump to a base pressure of 1027 Torr. Sputtering was performed with a direct current high voltage source (0–1 kV and 1 A) on a titanium target (99.98% purity). The titanium target was sputtered with a high purity argon–nitrogen mixture. The films were deposited on monocrystalline silicon (mc-Si) (111)substrates at different nitrogen partial pressures from 0.08 mTorr to 1.5 mTorr. Total pressure, power applied to target and substrate temperature were kept constant in all the experiments. Sputtering conditions are listed in Table 1.

Table 1
Deposition conditions for TiN thin films

DC power applied to target	(Watts)	250
Substrate temperature	(°C)	450
Total pressure	(mTorr)	4
N_2 partial pressure	(mTorr)	0.08, 0.1, 0.3, 0.8, 1.5
Target–substrate distance	(cm)	5

Firstly, quantitative analysis of samples was performed in a scanning Auger microprobe (Perkin Elmer PHI-595) operating with a resolution of *DE/E |0.3%.* Prior to analysis, all samples were Ar ion sputtered for 5 min in order to remove the native oxide on the surface. An Auger spectrum was taken for each sample in the 325 to 475 eV energy range. In addition, an XRD characterization was done using the Cu K_a X-ray radiation (l50.15405 nm) in an XRD Philips X'Pert-MPD. Only for a film deposited at 0.8

mTorr N_2 partial pressure (labeled as TEM sample), is an X-ray diffraction pattern presented in this work. Also, this film was prepared by the standard micropolishing and ion milling techniques for cross-sectional TEM and EELS analysis. TEM and EELS experiments were done in a JEOL 2010 TEM, with a Gatan 666 PEELS spectrometer.

Results and discussion

Fig. 1 shows Auger spectra of titanium nitride films deposited at different values of nitrogen partial pressures. For comparison, a Ti metal Auger spectrum is included in Fig.1.As the N_2 pressure is increased, the typical overlap between the $KL_{23}L_{23}$ Auger transition of N (|379 eV) with the respective $L_3M_{23}M_{23}$ Auger transition of Ti (|383 eV) appears. Similar results have been reported by Dawson and Tzatzov [7]. Also, the initial shape of the Ti $L_3M_{23}M_{45}$ Auger peak changes slightly as a function of nitridation of Ti. Quantification of the Auger data was done following the recipe developed by Dawson and Tzatzov.

Visual inspection of the golden color can be a first sign of titanium nitride compound formation. The golden color of TiN has been explained in terms of an ionic model [8, 9]. This characteristic was present on films deposited at 0.8 and 1.1 mTorr nitrogen pressure (Fig. 1e and f, respectively). Quantification of these samples, obtained by Auger spectroscopy, corresponds to values around the stoichiometric compound. Therefore, these results were considered in the selection of the sample deposited at 0.8 mTorr (N_2 partial pressure) as the sample for cross-section al TEM and EELS analysis.

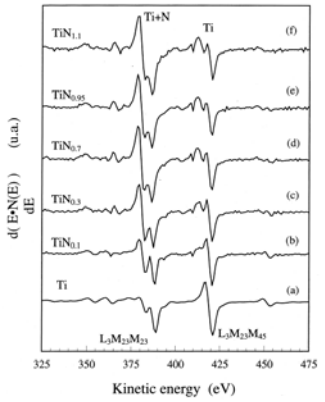

Fig. 1. Auger spectra of TiN films deposited at different partial pressures of N_2 (mTorr) (a) Ti, (b) 0.08, (c) 0.1, (d) 0.3, (e) 0.8, (f) 1.5.

The cross-sectional TEM image reveals a fibrous structure in which crystallites grow perpendicular to the substrate surface (Fig. 2). Since the crystallites develop close to each other, the density and other properties of the films are very similar to that of the bulk material [11]. The columnar microstructure was found only in sputtered films and is considered a result of bombarding the surface film with energetic particles during film growth.

An X-ray diffraction pattern from this sample, before its preparation for TEM analysis, shows only one TiN orientation (Fig. 3), k111l orientation. This indicates that polycrystalline columns must be highly k111l oriented. Oh et al. [12] reported that TiN films deposited by RF sputtering have the k200l orientation at the onset of deposition. After a critical thickness (above 4 mm for 50 W RF power), the films change to the k111l orientation. This change in orientation is associated with an increase in the strain energy of the films.

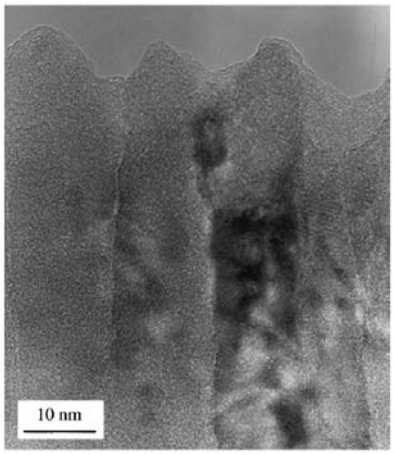

Fig. 2. Cross-sectional TEM image of the TEM-sample.

Increasing the DC or RF power, increases the energy of the particles bombarding the substrate surface during the sputtering processes [13]. This leads to an increase in the strain energy on the film [14]. In all the experiments, films were grown using 250 W power applied to the target, higher than the power used by Oh et al. [12]. Therefore, this condition promoted the deposition of k111l oriented films.

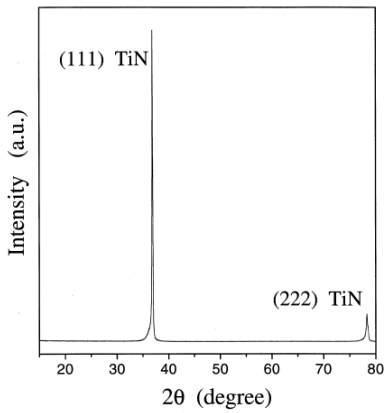

Fig. 3. X-ray diffraction pattern of TEM-sample.

Fig. 4 shows the energy loss spectrum corresponding to the titanium nitride sample (TEM-sam- ple) after subtraction of background and plural scattering. The features around the N K edge (400 eV) and the Ti L23 transition should be noted. The

elemental ratio, obtained from the N and Ti edges was N/ Ti50.95. The quantification method applied here is the standard process used in transmission electron microscopy [10]. This value is slightly different from the one obtained by Auger electron spectroscopy.

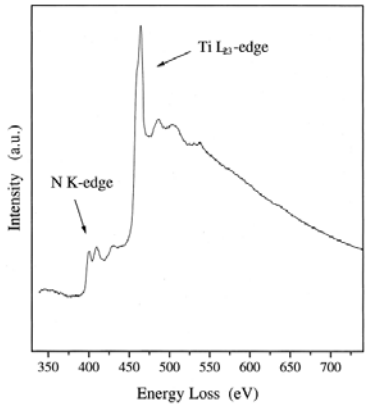

Fig. 4. Electron energy loss spectrum of titanium nitride thin film.

Finally, in Fig. 5 we present the atomic radial distribution function obtained through the Fourier transform of the fine structure in the Ti edge. Numerical values are in agreement with the expected values for the TiN structure. Radial distances are 0.19 nm for N atoms and 0.29 nm for Ti, first and second near neighbors, respectively. From the TiN fcc structure (NaCl type), the values expected are 0.21 nm and 0.29 nm for first and second near neighbors. The average difference between the numerical and expected values is 0.01 nm (|5%). In this case, the corrections due to phase shift were not applied.

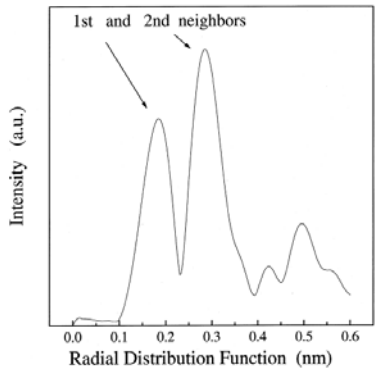

Fig. 5. Atomic radial distribution of N atoms around the Ti atoms.

Conclusions

We have performed a systematic characterization of TiN samples grown by DC reactive magnetron sputtering.

High resolution TEM and X-ray diffraction reveal a columnar polycrystalline structure with a k111l orientation. This particular orientation was ascribed to the bombardment of the substrate surface with energetic particles, sputtered atoms and sputtering ions.

The EELS results reflect the good quality of the TiN thin films grown by this method. The EXELFS analysis shows that the cross-sectional region has an atomic distribution as expected for the TiN structure. These numerical values are in good agreement with the known crystallographic values.

Auger spectra cannot quantify the atomic con- centration with precision. However, the EELS technique offers good high resolution quantification.

Acknowledgements

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