Available online at www.sciencedirect.com

ScienceDirect

Applied Surface Science 253 (2007) 5196–5202

applied surface science

www.elsevier.com/locate/apsusc

Surface analysis of the nanostructured W–Ti thin film deposited on silicon

S. Petrović [a,*], N. Bundaleski [a], D. Peruško [a], M. Radović [a], J. Kovač [b], M. Mitrić [a], B. Gaković [a], Z. Rakočević [a]

[a] *Institute of Nuclear Sciences – Vinča, P.O. Box 522, 11001 Belgrade, Serbia*
[b] *"Jožef Stefan" Institute, Jamova 39, 1000 Ljubljana, Slovenia*

Received 24 February 2006; received in revised form 30 October 2006; accepted 30 October 2006
Available online 17 December 2006

Abstract

The W–Ti thin films are deposited by the dc Ar^+ sputtering of W(70%)–Ti(30%) a.t. target on silicon substrates. The surface composition and structure of the thin film, previously exposed to air, was carried out. The surface structure was undertaken using grazing incidence X-ray diffraction (GIXRD), and compared to that of the thin film interior. The surface morphology was determined by the Scanning Tunneling Microscopy (STM). The surface composition and chemical bonding of elements on the Ti–W film were analyzed by X-ray photoelectron spectroscopy (XPS) and Low Energy Ion Scattering (LEIS). The measurements show that the overlayer of metallic oxides TiO_2 and WO_3 is formed. The first atomic layer is occupied by TiO_2 only, and its thickness is estimated to about 3.2 ± 0.4 nm. The strong surface segregation of Ti is triggered by the surface oxidation, which is confirmed by the thermodynamical considerations.

Keywords: W–Ti thin films; Surface segregation; GIXRD; STM; XPS; LEIS

1. Introduction

It is well known that W–Ti thin films suppress the interdiffusion between metal contact structures on silicon [1]. The most frequently used stoichiometry is 70:30 W:Ti a. t., where tungsten serves as the diffusion barrier (atomic diffusivities of most metals in tungsten is low) and titanium prevents grain boundary diffusion. The addition of titanium to tungsten also improves the corrosion resistance and the adhesive strength of the barrier [1,2]. Hence, their additional properties, such as thermomechanical stability, low electromigration and high corrosion resistance, make these films convenient as interdiffusion barriers for metallic contacts of semiconductor devices, especially in the case of high current densities and at increased temperatures [3].

The most probable diffusion mechanism through the barrier layers is the grain boundary diffusion, which is higher than the volume diffusion by orders of magnitude. For this reason, special attention has been given to the microstructure and to the concentration of impurities in the diffusion barrier layers, which govern grain boundary diffusion [4]. The addition of nitrogen and/or oxygen to the argon sputtering gas during the magnetron deposition of W–Ti thin film lowers the diffusion coefficient of a contact metal. The possible explanation of this effect is that the introduced gas atoms are collected at defect sites and grain boundaries, which contributes to blocking the open diffusion paths [1].

Different multilayered metal structures obtained by ion sputtering with W–Ti as a diffusion barrier layer has been investigated in [4]. The improvement of the diffusion barrier properties was achieved by exposing samples to air deliberately after the W–Ti deposition in order to contaminate them with oxygen [5]. According to the Auger Electron Spectroscopy (AES) depth profiling of the multilayered metal structures previously exposed to air, the concentration increase of O and Ti and decrease of W concentration took place. While the increase of the oxygen concentration on the mentioned interface is expected, the change of the Ti and W interface concentrations with respect to the thin film interior cannot be explained straightforwardly. Moreover, several questions arise

---

[*] Corresponding author.
E-mail address: spetro@vin.bg.ac.yu (S. Petrović).

0169-4332/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2006.10.077

about the structure, composition and topography of the W–Ti surface formed in this way, since it becomes a substrate for the deposition of metallic contacts.

Surface structure and composition of W–Ti thin film deposited by dc sputtering is analyzed in this work. The samples were exposed to the air after the deposition, i.e. before the analyses. This contributed, as it will be shown, to significant changes of the surface composition and provided important information concerning the oxygen interaction with W–Ti thin film at room temperature. The crystal structure of W–Ti thin films was analyzed by X-ray diffraction (XRD) using both, the standard geometry and grazing incidence in order to resolve the structure of the surface region from those of the thin film interior and the sample substrate. The surface morphology and the size of the surface agglomerates were determined using the Scanning Tunneling Microscopy (STM). The surface composition has been determined using X-ray photoelectron spectroscopy (XPS), as well as Low Energy Ion Scattering (LEIS). LEIS and XPS are complementary techniques for the surface analysis: XPS provides both the surface composition analysis and the chemical information, while the LEIS information depth is restricted to the first few atomic layers (which makes this technique particularly suitable for investigating the surface segregation phenomena). The composition of the thin film interior has been also determined, using XPS together with the Ar^+ ion sputtering.

2. Experimental

Thin films of W–Ti were deposited by dc sputtering (in Balzers Sputtron II system) of W:Ti 70:30 a. t. % target. The used substrates were (100) n-Si wafers, cleaned in an HF solution and in de-ionized water before mounting in the chamber. Before deposition, the sputtering chamber was evacuated by a turbomolecular pump, down to a final pressure 1×10^{-3} Pa. The substrate surfaces were cleaned by bias sputtering. The cleaning procedure included Ar^+ bombardment of substrates during 2 min at $I = 50$ mA and $V = 1$ kV. The sputtering deposition was performed at room temperature and the partial pressure of argon 1×10^{-1} Pa. Under such conditions, the deposition rate was approximately 0.095 nm s^{-1}. The thickness of deposited WTi thin films is 105 nm, measured by Talystep. After the deposition, the samples have been exposed to air at room temperature and relative humidity of about 50% for 10 days. We assume that equilibrium state at the sample surface was achieved during this period. The samples were then analyzed by different techniques.

The phase composition and crystalline structure of W–Ti thin films was recorded by grazing incidence X-ray diffraction. Cu Kα X-ray diffraction patterns were collected by a Bruker D8 Advance Diffractometer with parallel beam optics. The beam optics was adjusted by a parabolic Gobel mirror (push plug Ni/C) with horizontal grazing incidence soller slit of 0.120 and LiF monochromator. Angle 2θ in the range 30°–80° were scanned by a step of 0.02 degree in time sequence of 1 s.

The surface morphology of deposited W–Ti layer was analyzed by the STM NANOSCOPE III at room temperature and under atmospheric pressure. The STM image was obtained in constant current mode using a Pt(10%)Ir tunneling tip. Agglomerate size and mean surface roughness of the deposited W–Ti thin film were measured using the section analysis program in STM.

The W–Ti thin film was analyzed by XPS in the PHI XPS-TFA spectrometer. Monochromatized Al Kα X-ray beam was used for analysis of as-received surface and during the XPS depth profiling. The survey spectra and narrow scan spectra of Ti 2p, W 4f and O 1s were taken at resolutions of about 2.0 and 0.9 eV, respectively. The depth profile of the W–Ti film was obtained by ion bombardment of sample surface with 3 keV Ar^+ ions. A take-off angle of photoelectrons was 45° with respect to the sample surface. Concentrations of elements were calculated from peak areas using sensitivity factors provided by the instrument manufacturer.

LEIS experiments were carried out using the setup described in detail elsewhere [6]. He^+, Ne^+ and Ar^+ ions generated in a discharge-type ion source were accelerated to the desired energy in the range from 500 to 2000 eV, mass analyzed and focused onto the target inside the UHV sample chamber. The energy spread of the primary ion beam does not exceed few eV. Typical ion current density during the measurements was about 1 $\mu A/cm^2$. The scattered ions were energy analyzed using a 127° cylindrical electrostatic energy analyzer of 120 mm radius and a resolving power of about 140 FWHM. The incoming angle ψ and scattering angle θ can be continuously changed in the range from 0° to 90°. In all LEIS experiments specular geometry ($\theta = 2\psi$) was employed. The analyzed ions were post-accelerated in order to avoid the detection sensitivity dependence on the energy of detected ions. The sample has been cleaned by grazing incidence sputtering with He^+ ions with the current density of about 3 $\mu A/cm^2$ until the steady state was obtained. This way of surface cleaning was chosen in order to suppress the problem with the surface composition change during the standard cleaning procedure (which consists of heavy ion sputtering and sample heating cycles). During the experiment, the pressure in the chamber was lower then 5×10^{-7} Pa.

3. Results

3.1. XRD analysis

X-ray diffraction was used to reveal phase composition and crystal structure of the samples. Fig. 1(a) represents XRD spectrum of the 105 nm thick W–Ti film. In the presented spectrum two wide peaks can be observed: the first at about $2\theta = 40°$ of relatively low intensity and the second positioned at $2\theta = 70°$, which is more intense. Tungsten has a body centered cubic structure with a lattice parameter $a = 3.1648$ Å. The low intensity peak is attributed to W (1 1 0) plane situated at $2\theta = 40.264°$ (JCPDS card 04-0806). On the other hand, the lattice parameter calculated from the exact position of the mentioned peak amounts $a = 3.2237$ Å. The discrepancy between the measured lattice parameter and the value obtained in the referent measurements is due to the formation of the