Vacuum 107 (2014) 247–253

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Redox reactions in the Pt/TiO_2—WO_3/SiO_2 planar system

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ARTICLE INFO

Article history:
Received 15 October 2013
Received in revised form
14 February 2014
Accepted 18 February 2014

Keywords:
Metallic films
Barrier layer
Tungsten oxide
Reduction
X-ray Photoemission Spectroscopy
Synchrotron Radiation induced photoemission

ABSTRACT

The thermal behavior of the titanium—tungsten adhesive layer (30—70 at.%) deposited on a SiO_2 substrate followed by a thicker Pt layer was investigated. The resulting $Pt/TiW/SiO_2$ planar system was annealed under air or vacuum. Morphological and chemical characterizations at different stages of the annealing, as a function of several parameters such as treatment atmosphere, annealing temperature and thickness of the Pt film were performed through surface science analyses. When annealing under air, even at mild temperature (773 K), the whole interlayer oxidizes while a low amount of tungsten diffuses through platinum film. This phenomenon is related to tungsten oxidation which acts as the driving force leading to WO_3 ultra thin overlayer. On the obtained $WO_3/Pt/TiO_2$—WO_3/SiO_2 system, whatever subsequent vacuum annealing conditions are, the reduction process of surface tungsten oxide is revealed leading to $WO_{x<3}$ compounds on the top most layer. This reduction process is strongly connected to the temperature as well as the Pt amount, the reduction being more important when these parameters increase. For a 25 nm thick Pt and temperature higher than 773 K, the WO_3 reduction phenomenon can be huge reaching WO_2 stoichiometry.

1. Introduction

Platinum films are widely used in the field of microelectronics devices as well as on silica glass substrates for electrochemical applications including metal oxide gas sensors, and electrode thin films [1–7]. Due to their very good thermal and chemical stability and catalytic behavior, platinum-based systems are used under high temperature and/or harsh environmental conditions.

However, when platinum film is deposited on oxide materials such as SiO_2, film adherence is not enough to allow real industrial applications [5,6]. An ultrathin interlayer, often made of titanium [8] or titanium/tungsten alloy [9–12], can then be added in order to improve the coating-substrate adhesion. Titanium—tungsten layers have been investigated extensively for Al and Cu interconnects as well as silver or gold metallization and proved their ability to be good adhesive layer.

In the case of metals deposited on a TiW adhesive layer on silica [13], it was shown that these systems are stable up to 973 K when annealing is performed under vacuum. However, during annealing under air, an oxidation of the TiW layer as well as a break of the metallic layer can be observed from 723 K [14]. As most of the experiments have been done in inert atmospheres or under vacuum, our studies have been devoted to the thermal stability of the TiW adhesive layer under air for platinum films deposited on silica covered by a Ti—W interlayer [15]. One of these showed that, in spite of a huge improvement of the film adherence, further diffusion processes can modify the system. Especially, for annealing under air even at mild temperature (773 K), tungsten can diffuse through platinum and reach the system surface while the whole interlayer is fully oxidized. Actually, such a diffusion is related to tungsten oxidation which acts as the driving force leading to surface WO_3 ultra-thin precipitates forming a kind of new $WO_3/Pt/Ti$—W/SiO_2 system.

In addition, the WO_3/Pt system was widely studied in catalysis, these systems being used as an active bifunctional anode catalyst material for the oxidation of methanol, formic acid, CO or gas sensors for H_2, C_2H_4, C_2H_5OH [16–18]. Metals including ruthenium, osmium, tungsten and others have been shown to improve the catalytic activity of Pt either by modifying the surface chemistry to produce a bifunctional material or by modifying the electronic properties of Pt. In the bifunctional mechanism, the alloyed metals form surface oxides at much lower potential than Pt. By means of

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http://dx.doi.org/10.1016/j.vacuum.2014.02.014
0042-207X/

the electronic mechanism, alloying induces a different electronic structure resulting in a lower bond strength of the species adsorbed on Pt. The presence of tungsten oxide in Pt-based catalysts strongly modifies the platinum catalytic activity [19] leading to specific electronic interactions between platinum and tungsten oxide [20]. Especially, the reduction of WO_3 in WO_{3-x} can occur, induced by platinum which is well known to decrease metal–oxygen bonds and thus generate oxygen departure. Nevertheless, the induced reduction of WO_3 in WO_{3-x} is hard to reveal. In the case of seldom studied planar systems, such a reaction should be exalted and easier to reveal through regular surface science analyses.

In this study, Pt/Ti–W/SiO_2 system was performed through the deposition of 25 nm of metallic platinum on an intermediate titanium–tungsten layer intercalated between the SiO_2 substrate and the Pt film. The purpose of this work was to get some insight on redox phenomena occurring in the Pt/Ti–W/SiO_2 planar system during double thermal treatments, the first one being carried out under air and the second one under vacuum. Especially, this work is devoted to characterization of the film surface chemistry of the Pt/Ti–W/SiO_2 planar system during the annealing as a function of the annealing temperature and the thickness of the platinum layer. The system was investigated at different stages of the reaction through surface science analysis methods, i.e. X-ray Photoemission Spectroscopy (XPS) and Synchrotron Radiation induced photoemission (SR-PES). Transmission Electron Microscopy (TEM) and X-ray absorption near edge structure (XANES) experiments were also performed in order to get complementary information allowing the description of the whole system.

2. Experimental

Titanium–tungsten and platinum layers were deposited on amorphous SiO_2 substrates by RF magnetron sputtering. SiO_2 substrates were previously cleaned with a Piranha recipe [21]. A 5 nm thick titanium/tungsten layer was sputtered under Ar plasma, using a Ti–W (30–70 at.%) target. The Ar pressure and the RF power were 0.7 Pa and 50 W, respectively. A 25 nm thick platinum film was deposited on top of this layer using a platinum target (99.999% purity) under Ar atmosphere. The working pressure and the power were also 0.7 Pa and 50 W, respectively. All the materials were deposited at 638 K.

After deposition, the Pt/TiW/SiO_2 structure was annealed in a furnace under air at 773 K for an annealing time of 12 h. Subsequent annealing treatments were then performed on the resulting structure under vacuum at several temperatures (300–1023 K) and for different Pt film thicknesses (2.5–25 nm).

Morphological characterizations of the system were performed by Transmission Electron Microscopy (TEM) using a JEOL 2100 LaB6 with 200 kV acceleration voltage. The elemental chemical composition was determined by EDS in the electron microscope by means of a JEOL 2300 EDT. Cross-section samples were prepared by mechanical and ion thinning.

The chemistry of the film surface was analyzed through photoemission experiments on both Pt4f and W4f lines, using both classical X-ray Photoemission Spectroscopy (XPS) and Synchrotron Radiation induced photoemission (SR-PES). XPS experiments were carried out using a non monochromatized aluminum source (Al Kα radiation at 1486.6 eV) and a hemispherical EA125 analyzer (Omicron) with an analyzer slit of 1 mm and electron collection normal to the surface. The pass energy was 100 eV for survey spectra and 20 eV for Pt4f and W4f core level spectra. SR-PES experiments were performed on SX700 beamline at the ASTRID synchrotron source of the Institute for Storage Ring Facilities (Aarhus, Denmark). Primary photon energies can vary from 30 to 700 eV thanks to the use of a ZEISS SX700 monochromator. Electron detection was carried out normally to the surface using a VG CLAM II electron energy analyzer with a pass energy equal to 30 eV. The W4f line was recorded with primary photon energy equal to 160 eV. This photon energy corresponds to the maximum of the W4f photo ionization cross-section and the corresponding photoelectron kinetic energy is low enough to be as sensitive to surface phenomena as possible. The Pt4f line was recorded with primary photon energy equal to 200 eV allowing for Pt4f electrons the same kinetic energy as for W4f and thus the same sensitivity to the surface.

In addition, in order to get also chemical information on the whole layer and not only on the film surface, X-ray absorption near-edge structure (XANES) experiments were performed at the W M3 edge around 2280 eV. These measurements were carried out on the LUCIA beam line at the SOLEIL synchrotron. The detection mode was total electron yield.

3. Results and discussion

3.1. Oxidation of Pt/Ti–W/SiO_2 structure during annealing under air

The effect of annealing under air on the microstructure of Pt/TiW/SiO_2 structure was investigated through TEM observations. In the as-deposited state (Fig. 1(a)), the Pt/TiW/SiO_2 structure presents flat and clear interfaces, the Pt and TiW layers being distinguished by their contrast which are different because Ti–W layer is less dense than Pt. The measured thickness of Pt and TiW layers are close to 25 and 5 nm in good agreement with the deposition parameters. Direct measurements of the atomic composition of titanium/tungsten layer were performed using EDS analysis (spectra not shown here). EDS results obtained on the original layer evidence that the composition of titanium/tungsten layer is consistent with the one of the target, i.e. 30 at.% Ti:70 at.% W. Typical columnar growth for Pt layer with grains extending on the whole thickness of the layer, i.e. 25 nm, is observed. Regarding the TiW layer, a columnar structure with smaller grains of a few nanometers size is evidenced. After annealing under air at 773 K for 12 h (Fig. 1(b)), although all the interfaces as well as the columnar growth of Pt and TiW layers are not modified, a microstructural change is clearly revealed. The thermal treatment under air induces an important volume increase of the TiW layer, the thickness of this layer increasing from 5 to 15 nm. This expansion is consistent with the volume increase associated to the oxidation of TiW to TiO_2–WO_3, as it has been reported by Liehr et al. [14]. Considering the Ti/W atomic ratio of both the original TiW layer and the TiO_2–WO_3 oxides occurring during thermal treatment in air as well as the density of each phase, the volume of TiW and TiO_2–WO_3 layers can be calculated. The result is that such an oxidation process should induce a volume increase of a 2.9 factor. The surface composition of the as-deposited film is analyzed from XPS measurements and is compared to that of one annealed under air at 773 K. As can be seen in the XPS survey spectrum of the as deposited Pt/TiW/SiO_2 structure (Fig. 2(a)), the film surface is composed of platinum with a small proportion of oxygen and carbon coming from contamination. No sign of the presence of tungsten and titanium at the film surface is revealed. After annealing under air, in addition to the presence of Pt, C and O, tungsten is detected at the film surface, as evidenced by the appearance of peaks in the energy range of 31–41 eV corresponding to W4f core level spectra (Fig. 2(b), top curve). The W4f spectrum is formed of two components, corresponding to the $W4f_{7/2}$ and $W4f_{5/2}$ lines. The W4f peaks have binding energies at 35.6 and 37.8 eV. The chemical composition of WO_3 films has been widely investigated by core level photoemission spectroscopy. It has been documented that the location of W4f peak affords to know the oxidation state of W. The different oxidation states of W are represented by doublets shifted to higher binding energies from