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Thermal stability under air of tungsten–titanium diffusion barrier layer between silica and platinum

J. Nazon *, P. Simon, B. Domenichini, S. Bourgeois

Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS, Université de Bourgogne, 9 Avenue Alain Savary, Boîte Postale 47870, 21078 Dijon Cedex, France

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ABSTRACT

The present work investigated the thermal stability of tungsten–titanium diffusion barrier layers intercalated between SiO_2 substrate and platinum thin film. The resulting structures were annealed under air in the temperature range 400–600 °C for annealing times up to 100 h. Chemical and structural characterizations at different stages of the treatment evidenced several phenomena occurring during annealing under air, especially the complete oxidation of the adhesive layer, the diffusion of tungsten oxide through platinum film at particle boundaries as well as the sublimation process of tungsten oxide. The results of film surface chemistry and microstructure were correlated with diffusion phenomena.

1. Introduction

The request of industry for metallization processes in the field of devices and sensors, leading to systems able to operate at temperatures higher than 300 °C with no loss of the properties for long times is constantly increasing. Good performances imply the use of thin conductive films with good adhesion to the substrates as well as thermal stability, at least up to the highest processing temperatures.

A lot of metals, mainly aluminum, copper, gold or silver have been deposited as thin films [1–6] on silicon or SiO_2 substrates. Metal deposits often play the role of an electric contact. A current occurring problem, for instance in the case of Au–SiO_2 one, concerns the diffusion of the metal into the silicon dioxide substrate upon annealing and the poor adhesion of the metal film to the substrate [7]. These points are classically solved by using an intermediate layer acting as a diffusion barrier as well as a promoter of adhesion. As earliest metallization, Cr and NiCr alloy thin films were used for this purpose. However, they were found to be not stable enough against oxidizing environments at high temperatures [8]. Common barrier layers in use include Ti(N), Zr(N), Ta(N), Nb(N), etc. [9]. Among the best barriers, the multilayer structure Ti/Mo has been successfully applied to the Au–SiO_2 system. Moreover, in several metallization processes on silicon or SiO_2, the use of TiW solid solutions as barrier has proved to be successful. Tungsten–titanium barrier layers have been investigated extensively for Al and Cu interconnects as well as for silver or gold metallization [3–6]. It was shown, for example, that a silver thin film deposited on a Ti30/W70 layer on silicon is stable up to 600 °C under vacuum [10]: neither interdiffusion processes nor layer decohesion are observed. For temperatures higher than 650 °C, silver agglomeration occurs on the surface inducing a large increase of the resistivity. The same kind of behavior was observed in the case of different metals deposited on TiW–SiO_2 [11] revealing stable deposits up to 650 °C or 700 °C whether annealing is performed under vacuum. However, if annealing is carried out under air, an oxidation of the Ti–W layer is observed from 450 °C as well as a break of the metallic layer [12].

In this work, platinum was chosen as deposited thin film on silicon oxide: platinum is often used as electrode material mainly because of its chemical inertness even in a high oxidizing ambient. Besides, growth and properties of platinum thin films on different substrates have been widely studied because of potential applications in several fields [13,14]. Titanium was already used as intermediate layer in Pt/SiO_2 systems in order to promote adhesion of the Pt film to the silicon oxide substrate [15]. The influence of the annealing temperature on the Pt film microstructure and on titanium diffusion through the layer has been underlined [16] as well as the influence of TiO_2 interphase between the platinum and the silica upon the structure and the orientation of the Pt film [17]. Besides, concerning the adherence of platinum film, it was shown that the presence of tungsten oxide in Pt-based catalysts strongly modified the platinum catalytic activity [18] leading to specific electronic interactions between platinum and tungsten oxide [19].

* Corresponding author. Tel.: +33 3 80 39 63 32; fax: +33 3 80 39 38 19.
E-mail address: julien.nazon@u-bourgogne.fr (J. Nazon).

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In this study, an intermediate titanium–tungsten layer was deposited between the substrate and the Pt layer. As most of the previous studies about the thermal stability of Ti–W barrier layers have been carried out under inert atmospheres or vacuum, this work is devoted to annealing treatments under air in 400–600 °C range. The system was investigated at different stages of the reaction mainly through Transmission Electron Microscopy (TEM) and X-Ray Photoelectron Spectroscopy (XPS) analyses. The purpose of this work is thus to get some insight on diffusion phenomena and interfacial reactions occurring at the Pt/Ti–W/SiO_2 interfaces for annealing under air. Actually interdiffusion and related mass transport can be beneficial from the viewpoint of promoting adhesion as long as other properties are not being damaged.

2. Experimental

Titanium–tungsten and platinum layers were deposited onto amorphous SiO_2 substrates by RF magnetron sputtering. Amorphous SiO_2 substrates were previously cleaned with a Piranha recipe [20]. A 5 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 these layers using a platinum target (99.999% purity) under an Ar atmosphere. The working pressure and the supply power were 0.7 Pa and 50 W, respectively. All the samples were deposited at 365 °C.

Annealing treatments were performed in a furnace under air at temperatures of 400 °C, 500 °C and 600 °C for times between 1 min and 100 h.

Morphological, crystallographic and chemical characterizations of the system were performed by Scanning (SEM) and Transmission (TEM) Electron Microscopies. SEM was performed by means of a Jeol JSM-7600F field emission scanning electron microscope operating at 30 kV. This apparatus was also equipped with a LABE backscattered electron detector analyses. Specimens for cross section TEM observations were prepared by standard procedures of cutting, gluing, mechanical grinding using Gatan Dimple Grinder and Precision Ion polishing System. The analyses were performed using a JEOL 2100 LaB_6 with 200 kV acceleration voltage. The elemental chemical composition was determined by EDS in the electron microscope by means of a JEOL 2300EDT.

Samples were analysed by photoemission using a non monochromatized aluminum source (Al Kα radiation at 1486.6 eV). The basic pressure in the experimental vessel was better than 2×10^{-10} hPa. Photoelectrons were collected by a hemispheric EA125 analyzer (Omicron) with an analyzer slit of 1 mm. The pass energy was 100 eV for survey spectra and Pt4f and W4f were also recorded at a pass energy of 20 eV. The electron collection was performed normally to the surface. Shirley background subtraction was used for peak area measurements giving line intensities. The area of the W4f line was measured within a window of about 20 eV including the $4f_{7/2}$ and $4f_{5/2}$ components. A window of about 15 eV was used for Pt4f peak areas, so that the two components associated with $4f_{7/2}$ and $4f_{5/2}$ spin orbit doublet were taken into account.

3. Results

3.1. Characterization of the as-deposited SiO_2/Ti–W/Pt structure

TEM observations of the SiO_2/Ti–W/Pt in the as-deposited state are shown in Fig. 1. The two interfaces are flat and clear, the Pt and Ti–W layers being distinguished by the different contrasts. The thicknesses of Pt and Ti–W layers are close to 25 and 5 nm, these values being perfectly in accordance with deposition parameters. Direct measurements of the chemical composition of titanium–tungsten layer were performed using EDS analysis (not shown here). EDS results obtained on film samples evidenced that the composition of titanium–tungsten layer is consistent with the one of the target, i.e. 30 at.% Ti:70 at.% W. TEM observations also do not reveal any cracks of the layers. EDS depth profiles were performed from sample surface to silica substrate. The depth profiles of Pt, W, Ti and Si demonstrate that no interdiffusion process occurs at the SiO_2/Ti–W and Ti–W/Pt interfaces. It can also be seen that the Pt film exhibits a kind of columnar growth perpendicular to the substrate surface as evidenced from the coexistence of dark and light contrast areas, consisting in grains of 15–25 nm size in diameter. The Ti–W layer presents also a columnar structure with smaller grains of a few nanometers size. Such a microstructure is commonly observed in sputtered films as predicted by the model of Movchan and Demchishin [21] as well as the one of Thornton [22]. This columnar microstructure is associated with inter-column voids which can act as short-circuit diffusion paths in solid materials, by which means of atom transport occur [23].

The surface composition of the film was analyzed using XPS (Fig. 2). The XPS survey spectrum for the as-deposited SiO_2/Ti–W/Pt system reveals that the film surface is composed of platinum (presence of Pt4p, Pt4d and Pt4f lines) as well as oxygen (O1s) and carbon (C1s) coming from contamination. The Pt4f core level spectrum before annealing shows two components associated with $4f_{7/2}$ and $4f_{5/2}$ spin orbit doublet with binding energy at 72.1 and 75.4 eV. These values as well as the asymmetric shape of the peaks are characteristic of metallic Pt. Considering the O1s and C1s photoemission spectra, the surface contamination due to hydrocarbons is evidenced by the components at 532 eV and 284.5 eV which are characteristic of the O–C and C–C bonds, respectively. Furthermore, it can be seen that neither tungsten nor titanium are detected at the sample surface, which is in good agreement with the absence of interdiffusion phenomena previously observed through TEM analysis.

3.2. Thermal stability of the SiO_2/Ti–W/Pt structure during annealing under air

The effect of annealing treatments on the SiO_2/Ti–W(5 nm)/Pt metallization scheme was firstly studied through the evolution of the relative intensities of Pt4f and W4f lines recorded by XPS. For instance, the Pt4f and W4f core levels spectra of the sample annealed at 500 °C as a function of annealing time are shown in Fig. 3. Shape and position of Pt4f peak do not change upon annealing. Considering the W4f core level spectra, tungsten is revealed in the top most layers of the sample after an annealing time of 10 min at 500 °C under air. Two components associated to $W4f_{7/2}$ and $W4f_{5/2}$ spin orbit doublet having binding energy at 35.6 and 37.8 eV are then recorded. Such a W4f doublet is shifted by about 5 eV towards higher binding energy relative to the metal state. If compared with the literatures [24,25], this doublet can be attributed to photoelectrons emitted by tungsten for stoichiometric WO_3. By increasing the annealing time, the position of W4f peaks did not obviously change, which indicates that no reduction of tungsten oxide is observed. Furthermore, whatever the annealing conditions (temperature, time), no additional component arises in the Pt4f or W4f core level spectra. It should be also noticed that no titanium is detected at the sample surface whatever the annealing conditions are. Hence, for long annealing time, the top most layers of annealed film are composed of WO_3 and metallic platinum only (Fig. 4).

The evolution of tungsten oxide amount in the top most layers during annealing was evaluated from the XPS W4f and Pt4f core level spectra and peak area measurements. The evolution of W/Pt intensity ratio as function of the annealing time is reported in