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ScienceDirect

Journal of Non-Crystalline Solids 353 (2007) 1844–1848

JOURNAL OF
NON-CRYSTALLINE SOLIDS

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Structure of copper-doped tungsten oxide films for solid-state memory

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Abstract

Copper-doped WO_3 films, which are an active media for programmable metallization cell memory devices, are studied. The highlights of this study are the intercalation products forming on the interface between the WO_3 and Cu during thermal evaporation and also after thermal or photothermal diffusion of Cu into WO_3 films. The diffusion profile is established using Auger spectroscopy. Further characterization is provided using Raman spectroscopy which gives evidence for formation of products with a lower valence state related to W and oxidation products related to Cu. The composition of the intercalation products containing Cu is confirmed using X-ray diffraction which shows the formation of copper oxides and tungstates.

PACS: 42.70.Ce; 78.30.–j; 61.72.Dd; 82.80.Pv

Keywords: Phonons; Raman scattering; X-ray diffraction; Microcrystallinity

1. Introduction

Tungsten is a widely accepted material in the microelectronics industry, especially in its application in multilevel interconnects. Tungsten plugs provide the required vertical connection between the horizontally running wiring which is now made of copper. In a typical Back End of the Line (BEOL) process [1], the interconnects made of tungsten plugs and copper offer excellent opportunities for the development of a memory cell, thus increasing the capacity of the unit's memory storage due to the introduction of Programmable Metallization Cell (PMC) memory devices [2] fabricated on the tungsten plugs. These devices are composed of a thin film of solid electrolyte sandwiched between a copper anode and an inert cathode. Under the influence of an electric field, the electron current from the cathode reduces an equivalent number of Cu-ions as injected from the anode and a metal-rich electrodeposit is thereby formed in the electrolyte. The electrodeposit is electrically neutral and stable; however, applying a bias with opposite polarity can reverse the formation process. The reverse ion current flows until the previously injected Cu oxidizes and deposits back onto the electrode, which was the initial source of the metal. Thus, the resistivity increases again until the high value characteristic for the solid electrolyte is reached [3].

Since tungsten has a lower electronegativity than Cu [4], it could be successfully used as an 'inert' electrode in the construction of the PMC devices. Tungsten also offers one more degree of compatibility and ease of processing within the overall structure of the integrated circuit when metal-doped WO_3 is used as a solid electrolyte because one can use the W as the starting material for the electrolyte. Doping WO_3 with Cu and establishing a Cu oxidizable electrode in the PMC structure contributes towards one more degree of technological simplicity.

WO_3 is known to easily form tungsten bronzes [5]. They are reduced phases with the general formula A_xWO_y where

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doi:10.1016/j.jnoncrysol.2007.02.054

A is typically an alkali metal but can also be some other electropositive metal, and x is less than 1. In the case of thin films, the structure is not as well organized as in crystals where specific tunnels exist [5] but niches and channels are still available where metal and in particular Cu atoms could be accommodated. Scientific and technological interest towards WO_3 films stems also from the fact that they possess electro- and photo-chromic effects [6]. It is believed that photochromism can be explained by the double-charge-injection model [7]. By the injection of H ions and electrons into a WO_3 lattice, a tungsten bronze structure (H_xWOWO_3, $0 < x < 1$) is formed and then W^{6+} is partially reduced to W^{5+} in tungsten oxide hydrate or W^{4+} in 12-tungstates by electrons occupying the empty W5d orbital due to the electron localization effect. In the presence of electronegative metal in the WO_3 sublattice, electron injection can be initiated by the metal and this opens new perspectives into the diffusion mechanism. This effect has a very important consequence for PMC technology as it suggests that there is a good opportunity to control the process of metallization of WO_3 by which the optimum conductivity of the material for the operation of the devices can be achieved. This perspective is the driving force for the study reported in this work that is related to research on the formation of WO_3 thin films due to thermal evaporation. It complements our previous research related to the formation of WO_3 films using wet or plasma oxidation [8] that were applied for the formation of PMC devices. The present research is related to the creation of specific doped products using standard thermal doping or photo-assisted doping to form a solid electrolyte based on WO_3 and characterization of these products using Field Emission Scanning electron microscopy (FESEM), Auger (AES) and Raman spectroscopies, as well as X-ray diffraction (XRD).

2. Experimental

The studied films were evaporated on Si wafers covered with a TiN film which provides a barrier to Cu diffusion ensuring that Cu diffuses only into the WO_3. Sandwiches of 100 nm each of Cu and WO_3 on top of it were evaporated using electron-beam-assisted heating for the thermal sublimation of high-purity Cu and WO_3 pieces produced by Cerac, and the thickness was controlled using a quartz crystal monitor. The evaporation rate was 2 Å/s while the substrates were rotated to ensure uniform coating of the films.

Two different means of diffusion processes were used: (i) thermal diffusion, for which a convection oven set at 135 °C was used and since the chamber of the oven did not permit external light to interfere with the process, it could be considered as a purely thermal diffusion. The temperature was chosen to be 135 °C because this coincides with a number of technological requirements, e.g. this is the temperature at which the photoresist begins to denature. Hence the treatment time was restricted to 30 min; (ii) photo-thermal diffusion. To achieve photo-thermal diffusion, a setup involving a commercially available lighting source of a 500 W tungsten halogen lamp assembly was used. The temperature was 135 °C. Photo-thermal diffusion was also carried out for 30 min.

The films were characterized using the following methods: (i) The morphology was characterized using a Hitachi S4700 field-emission scanning electron microscope at an acceleration voltage of 15 kV and emission current 10 μA. (ii) AES was carried out in a Physical Electronics SAM 590 scanning Auger microprobe surface analysis system. Secondary electron excitation was obtained via a 5 kV electron gun with a beam spot size of 0.5 μm. Depth profiling was accomplished by coordinating the AES analysis with Ar^+ ion gun etching in the sample surface region of interest. (iii) Raman spectra were collected using an Acton Spectroprobe-275 with a Coherent Ar^+/Kr^+ ion laser for providing 488 nm and 514 nm excitation that was detected with a liquid nitrogen cooled CCD camera. To reveal details about the different modes that exist, deconvolution using Lorentzian expressions was carried out. (iv) The XRD was accomplished with a Philips X'pert MPD diffractometer with Cu Kα radiation $\lambda = 1.54$ Å). In order to cover more lateral depth and to collect better signal from the thin film, the experiment was run at a constant source angle of 1°, while the detector was scanned from 10° to 95°. For these particular experiments, the WO_3 films were thicker than 500 nm to prevent the X-ray beam seeing the underlying Cu film, leading to misleading results.

3. Results

The intercalation process is very easy accessible in this system as we have established from the AES study of the films – Fig. 1. Note that the surface of WO_3 is where the measurement begins (from the left side) and the point at which the Cu concentration saturates can be treated as the boundary between the WO_3 and Cu. It is obvious that some copper diffusion occurs even during the film preparation and under these conditions some copper appears on the surface of the WO_3 film. A marked difference is noticed in the profile when Cu is photothermally diffused, indicated by an almost 'step-like' diffusion profile characteristic of diffusion along a charge front by ionic species. In the case of thermally diffused Cu, it follows a profile resembling an error-function, indicating a thermally activated diffusion from an infinite source of the impurity. Also visible on the thermal and photo-thermal diffusion profiles is a significant pile up of Cu at the surface.

The Raman spectra of the initial WO_3 films are shown in Fig. 2. The undoped film which was maintained at room temperature shows a pronounced peak at 926 cm^{-1}. The main peak at 932 cm^{-1} has a shoulder that can be deconvoluted in two peaks at 838 and 729 cm^{-1}, tracing their origin back to the stretching modes of the O–W–O bond. Since the considered WO_3 film is amorphous, the bending mode of the O–W–O bond is presented with a very wide peak