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Effect of in situ ultrasonic treatment on tungsten surface oxidation

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Abstract

In the present study we report on the influence of in situ ultrasonic treatment (UST) on the oxidation of tungsten surface with low-temperature oxygen plasma. We observed that in situ ultrasonic assisted oxidation leads to the substantial change of crystallinity and decreased surface roughness after oxidation. TOF-SIMS profiling and transmission electron microscopy study show significant decrease of the oxide thickness and distinctly sharper WO–W interface upon the action of acoustic vibrations. The stoichiometry of the formed films was evaluated from O1s and W4f XPS peak ratio and was found to be independent on the presence of ultrasonic treatment.

Keywords: Tungsten oxide; Plasma processing; Surface structure; Morphology; Roughness; Topography; Crystalline–amorphous interfaces

1. Introduction

Optically active thin films have attracted considerable attention with respect to their properties that can alter as a function of changes in external condition [1–4]. Materials with controllable transmittance, reflectance or absorptance possess a great technical relevance because of their high potential for applications. Most of the investigations on inorganic materials are documented on oxide films of transition metals. Among them the tungsten oxide has been studied in much greater detail than any other chromogenic material [4].

In general, the as-deposited state is different in terms of density, composition, atomic structure

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(amorphous, nanostructured clusters, polycrystalline, crystalline etc.), depending on the deposition technique [5,6]. It is suggested that electrochromic properties strongly depend on the oxide structure, the porosity or density of the oxide films, water molecules in the films, and its stoichiometry (see for example [1,4] and references therein).

Sonochemistry is a very interesting field of modern physical chemistry. Ultrasonic waves can enhance chemical reactions due the dispergation of solid components or catalyst, intensive mixing, degassing etc. Even with the comprehensive treatise on sonochemistry published by Margulis [7], there exist a limited number of conclusive results where the understanding of physical mechanisms was achieved. Over the last few years sonochemical reactions in non-liquid medium have been intensively investigated. Ostapenko [8] has demonstrated that ultrasound treatment (UST) enhances diffusion of hydrogen in thin polycrystalline Si films. UST applied to plasma-hydrogenated films improves the homogeneity of recombination and transport properties. Krüger et al. [9] reported about enhanced amorphization of silicon during UST argon implantation. The influence of ultrasound is discussed in terms of its interaction with point defects and ultrasonic-stimulated enhanced diffusion of interstitials.

In this work we have studied the influence of in situ applied acoustic waves on tungsten oxide formation in the reactive oxygen plasma. In such non-equilibrium processes the target atoms are excited and defect complexes are unstable or highly metastable. Such systems are very sensitive to ultrasonically induced lattice distortions that can promote a change in kinetics of chemical reactions.

2. Experimental details

Thin (200 nm) tungsten films were deposited by sputtering of the W target using standard PVD method on p-type silicon (100) wafers (resistivity 10 Ω cm). The initial tungsten film is nanocrystalline with an average grain size of 55 nm which is characteristic for films deposited with sputtering. The oxidation of the tungsten surface has been performed in a low-temperature oxygen plasma at a pressure of 0.5 Pa (5×10^{-3} mbar) in the same experimental chamber without breaking the vacuum, resulting in thin surface oxide film formation. All depositions and plasma treatments were done at room temperature. The ultrasonic vibrations were generated in the sample by operating the transducer in a resonance vibration mode at resonance frequency of 5 MHz and acoustic power of 1 W cm^{-2}.

In order to avoid the contamination of the overlayer and possible change of stoichiometry the samples were transferred into the XPS measurement chamber without breaking the vacuum. The XPS measurements were done on a VG ESCALAB 210 spectrometer using monochromatized AlKα radiation (1486.6 eV) with an energy resolution of better than 0.5 eV. The energy position of the spectra were calibrated with reference to the $4f_{7/2}$ level of clean gold sample (positioned at 84.0 eV binding energy). To determine the contribution of oxide and metal components as well as to obtain peak positions, a fit procedure was applied. The peak shape itself is described by a Doniach–Sunic function [10], and a Shirley background [11] is used to approximate the background contribution which arises from the inelastically scattered photoelectrons.

Low-energy TOF-SIMS depth profiling was performed with a TOF-SIMS IV system in dual beam mode with 0.6 keV Cs^+ sputtering and 10 keV Ar^+ primary ion beam for secondary ion generation. The surface morphology of the formed oxide films were assessed by scanning electron microscopy (SEM). SEM micrographs were obtained with Philips XL 30.

In an attempt to obtain more accurate information about the structure and thickness of the tungsten oxide film, a thin (100 nm) lamella has been cut from the sample using the focused ion beam (FIB) technique and investigated with transmission electron microscopy (TEM). The lamella has been prepared using a FEI 235 dual beam system. To protect the tungsten oxide film, as a first step, a platinum layer of about 30 nm thickness was deposited by electron beam induced decomposition of a platinum precursor gas injected onto the sample, followed by an ion beam deposited platinum layer of another 150 nm thickness.

Subsequently, the lift-off procedure described in [12] has been applied. The TEM analysis was done using Philips CM 30 with an EDX (EDAX DX4), operated at 200 kV accelerating voltage.

3. Results and discussion

Fig. 1a shows SEM micrograph of oxidized tungsten surface without UST. The normal, i.e. without acoustic waves, oxidation results in formation of uniform oxide film and does not change the surface morphology. On the other hand in situ induced ultrasonic vibrations lead to substantial change of crystallinity and formation of a flat films (Fig. 1b). The surface roughness measured with AFM and defined as arithmetic average of the absolute values of the surface height deviations is found to be ~2 nm for the normally oxidized sample, whereas that of oxidized with UST is found to be ~0.5 nm.

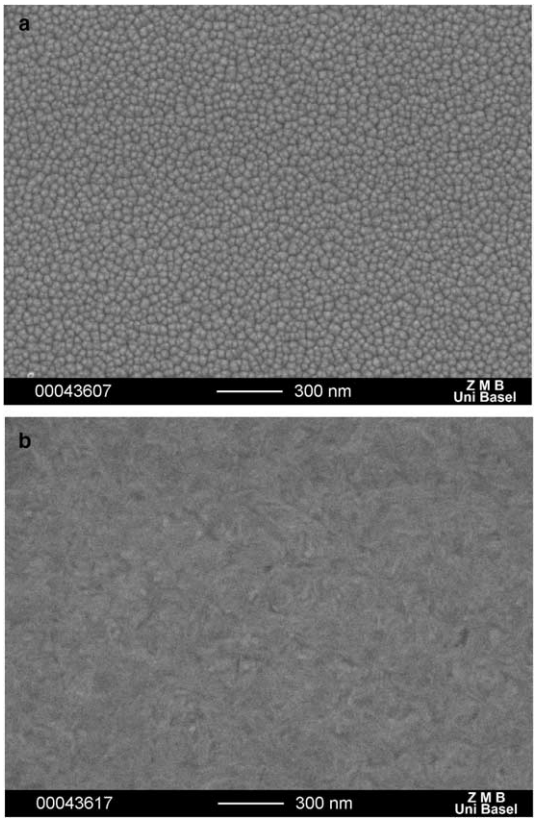

Fig. 1. SEM micrograph of the oxidized tungsten surface: (a) without ultrasonic filed, (b) with in situ applied ultrasonic vibrations.

The photoemission spectra of W4f core-level doublet of both oxides are presented in Fig. 2. Both samples have similar photoemission spectra, which consist of two doublets: one at binding energy 35.38 eV for the $W4f_{5/2}$ and spin–orbit splitting energy Δ of 2.14 eV, and a second doublet that is related to the metallic underlayer at binding energy of 31.23 eV for the $W4f_{7/2}$ with the same spin–orbit splitting energy Δ. The ratio between integrated intensities under the oxide related peak and that of the metal is found to be 12.4. At the same time, the ratio oxide/metal area for the US assisted oxidation is 6.1, indicating thinner oxide layer in latter case.

The stoichiometry of the formed films was evaluated from O1s and W4f XPS peak ratio taking into account the ionization cross-sections for respective lines and was found to be the same for film obtained with and without acoustic field and equals to 3.01 ± 0.07.

On Fig. 3 the depth distribution of WO_3 fragment ion of both samples measured with TOF-

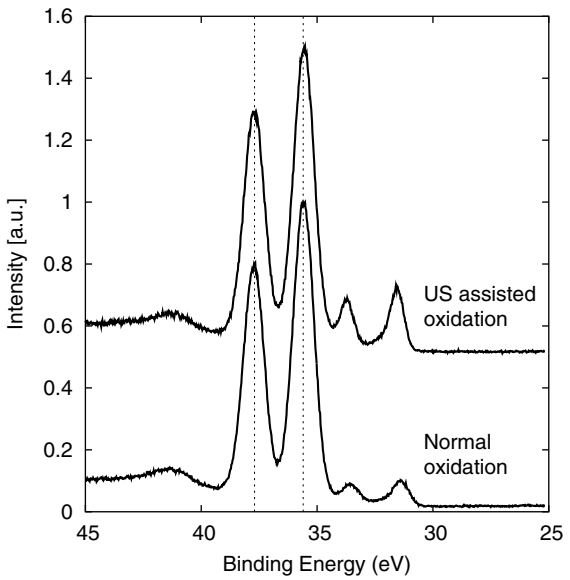

Fig. 2. XPS W4f spectra for two oxidation techniques.

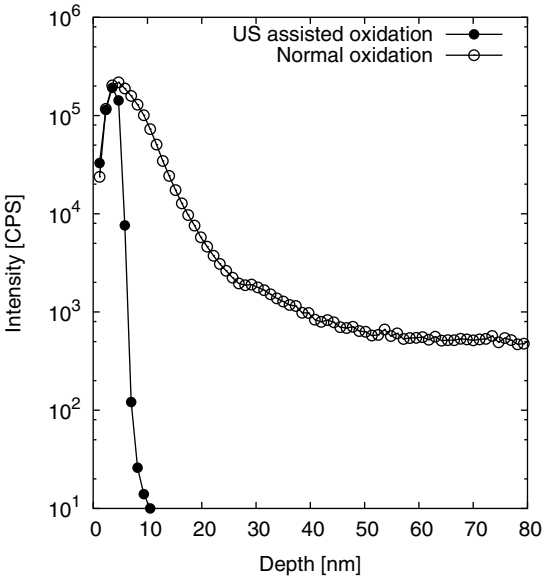

Fig. 3. Depth profile of WO_3 fragment ion of normally and US assisted oxidized films.

SIMS is shown. For the oxidation without UST the concentration of WO_3 shows slow decrease of intensity. The thickness was evaluated from maximum secondary ion yield of WO_2 and WO fragment ions (not shown here) which characterizes change of tungsten atom environment that takes place at the interface and was found to be about 12 nm. At the same time for the US assisted oxidation the oxide thickness comprises only ~5 nm. It is also evident that acoustic waves in the sample result in distinctly different distribution of WO_3 fragment ion. That could be attributed to the different surface structure of the films observed with SEM or alternatively to a formation of various WO–W interfaces. The latter assumption receives support from TEM analysis, those pictures are shown on Fig. 4a and b for normal and UST oxidation, respectively. The oxide film obtained without acoustic vibrations (Fig. 4a) is about 13 nm thick and does not show clearly defined WO–W interface. At the same time UST oxidation leads to the formation of thin (~4 nm) film with pronounced oxide–metal interface (Fig. 4b).

The microscopic details of the oxidation mechanism under the influence of ultrasonic vibrations are

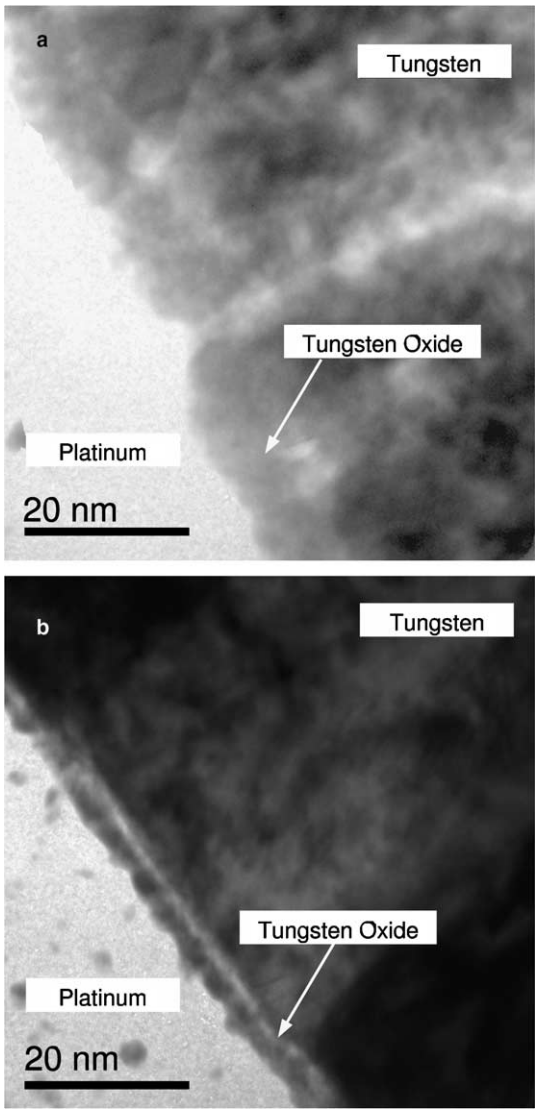

Fig. 4. TEM micrographs (bright field image mode) of the oxidized tungsten surface: (a) without ultrasonic treatment, (b) with in situ applied ultrasonic vibrations.

not clear yet. The creation of stretched and compressed areas in the metal film stimulated by acoustic waves may be responsible for different oxidation kinetics. Indeed, the mechanical stresses play an important role in defect creation and their motion during target bombardment with energetic ions [13,14]. Accumulation of vacancies at the near-surface region and enhanced creation of amorphous

phase upon the action of ultrasound during argon implantation in silicon has also been shown by Krüger [9]. Hence it follows that in the absence of ion irradiation the acoustic field alone should not lead to any substantial change in crystal. This is confirmed by applying ultrasonic post-treatment to normally oxidized sample. After the treatment no change in surface morphology and oxide thickness has been observed. From the other side the acoustical vibrations are partially transmitted into the plasma leading to the change of plasma properties, such as electron and ion temperature, plasma density etc. Furthermore, acoustic field may significantly affect the thickness of sheat region, also known as a dark space. The dark space thickness is pressure dependent and its increase will cause an increase of the the ion's kinetic energy having a profound impact on physical sputtering yield. The ultrasonically induced change of plasma temperature may also lead to different chemical reactivity of the agent–surface combination affecting kinetics of oxidation reaction [15]. Identification of the mechanism responsible for the observed effect will be a subject of further investigation.

4. Conclusions

In summary we have shown that ultrasonic treatment applied to the oxidation of tungsten is beneficial in improving flatness and homogeneity of the formed oxide film. The physical model of oxide formation is discussed in terms of the interaction of ultrasonic waves with defects in metal as well as with the oxidizing plasma. The properties of the films obtained with UST oxidation might be promising for many applications and will be a matter of the future research.

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