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Oxidation and reduction of thin Ru films by gas plasma

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Abstract

The oxidation and reduction of Ru thin films grown on a Si(1 0 0) surface were studied by X-ray photoemission spectroscopy (XPS). Ru thin films were oxidized with O_2 plasma generated by an rf discharge, and their XPS spectra were measured. The spectra were decomposed into several components for Ru suboxides attributable to different stages of oxidation. After sufficient exposure to oxygen, a stoichiometric rutile RuO_2 layer was found to have formed near the surface. Thermal annealing at 500 K resulted in a thicker RuO_2 layer. Experiments demonstrated that the Ru oxide layer can be removed by H(D) atoms via the desorption of water molecules.

Keywords: Ru; Oxidation; Reduction; Surface reaction; Plasma treatment

1. Introduction

Ru is a promising element for coating Mo/Si multilayer mirrors for extreme ultraviolet (EUV) lithography because it is highly resistant to oxidation. However, during long exposure to EUV light, a Ru thin film is eventually oxidized in the presence of oxygen and/or water molecules, resulting in lower mirror reflectivity. Madey et al. [1] reviewed recent progress in research on the surface oxidation of single-crystal Ru from the standpoint of its use for coating mirrors for EUV lithography. The decomposition by energetic electrons or photons of water molecules that have adsorbed to Ru is a critical issue related to making EUV lithography a practical tool. In the lithography system, oxygen radicals can form by the EUV-induced photolysis of oxygen and/or water molecules, thereby accelerating the oxidation of a Ru coating.

The surface oxidation of semiconductors by O atoms has been extensively studied in relation to Si electronic devices [2]. However, the mechanism involved in the oxidation of the surface layer of Ru by O atoms has been studied less than the one involving O_2 molecules. The oxidation mechanism has been investigated rather for the purpose of devising better catalyzers for solar energy conversion and for understanding the oxidation of CO in fuel cells [3–9]. Analysis of the surface of single-crystal Ru(0 0 0 1) by X-ray photoemission spectroscopy (XPS) is often used to elucidate the early stages of oxidation [4,9–13]. The Ru (3d) peak of a core-level photoemission spectrum obtained from a Ru(0 0 0 1) surface oxidized by O_2 consists of several components arising from Ru suboxides, which are characterized by an O coordination number of less than 6, the number for stoichiometric rutile RuO_2 crystal. They are distinguished by a chemical shift from the Ru (3d) bulk component, which has a binding energy of about 280 eV. The presence of chemically shifted peaks suggests that various types of Ru suboxides form depending on the extent of oxidation or oxygen coverage. Stoichiometric rutile RuO_2 layers have been reported to form at high temperatures of around 500 K [9,10].

The removal of an oxide layer on a Ru film is of technological relevance to EUV lithography because such a layer reduces the reflectivity of an EUV mirror. An oxide layer can, in principle, be removed from a Ru(0 0 0 1) surface by heat treatment at a high temperature because temperature-programmed-desorption (TPD) spectroscopy has shown that oxygen molecules do, in fact, desorb from the surface [14,15]. However, such a high temperature is not suitable for practical EUV lithography because it causes intermixing of the layers of the Mo/Si multilayer coating on an EUV mirror,

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thereby degrading the reflectivity. Recently, it has been shown that oxide on a Ru thin film can be removed even at room temperature by H atoms generated with a hot W filament [16]. Thus, atomic-H cleaning is a very promising and practical method for the in situ removal of oxide from Ru-coated optics for EUV lithography. The purpose of the present study was to clarify the process by which a Ru thin film is oxidized when exposed to oxygen plasma. XPS was used to reveal how the oxide structure depends on exposure conditions. In addition, hydrogen plasma treatment was demonstrated to be an effective way of removing oxide from a Ru film; and in *in situ* mass spectrometric experiments showed that the oxygen removal reaction proceeds via the desorption of water molecules.

2. Experiments

Ru thin films (thickness: 18.6 nm) were deposited on Si(1 0 0) surfaces by means of the magnetron sputtering of solid bulk Ru in a vacuum. The samples were then mounted on a sample holder attached to a manipulator that enabled the sample position along the *x*-, *y*- and *z*-axes as well as the polar angle to be set. Since as-obtained samples were used without any cleaning, native oxide was present on the surface.

We employed two plasma surface reaction systems: In system A, *ex situ* X-ray photoemission spectroscopy (XPS) was used to study the process by which plasma oxidizes a Ru film; and in system B, *in situ* mass spectrometry was used to study the reduction process for Ru oxides.

System A consists of a surface reaction chamber equipped with an rf (13.56 MHz) discharge plasma gun, which ran at a power of 150 W. In order to generate H or O radical atoms, either H_2 gas mixed with Ar gas or pure O_2 gas was introduced into the reaction chamber at a constant pressure of 4×10^{-4} Torr and an rf plasma was generated. The distance between a sample and the rf plasma source was about 5 cm. A Ru thin film was oxidized by exposure to O atoms for 1, 5, 10, 20, 30, or 35 min. Immediately after the 5-min oxidation, H atoms were admitted to the surface for 5 or 10 min to remove the oxides. Samples thus prepared were kept in a desiccator evacuated to 1×10^{-3} Torr until transfer to the XPS machine. XPS spectra were measured with the Mg Kα line (1243.6 eV) at a base pressure of 1×10^{-9} Torr. The pass energy for the analyzer was 0.95 eV. The background signals in the XPS spectra were subtracted by means of Shirley's method [17]. Then, the XPS spectra were decomposed by a curve-fitting method with Gaussian/Lorentzian functions with an exponential tail to account for the peak asymmetry arising from core-hole coupling [18]. Although the XPS data are plotted in arbitrary units, the intensities of the components are comparable among the figures presented in this paper.

System B was used to *in situ* measure the amount of desorbed water molecules with a quadrupole mass spectrometer (QMS) during the exposure of an oxide surface to D atoms. We used D atoms instead of H atoms because signals from desorbed H_2O molecules were buried in the background signal for H_2O. In order to reduce the background pressure, a D beam generated by an rf plasma discharge of D_2 gas mixed with Kr gas (50:50 in pressure) passed three differentially pumped chambers before being admitted to the surface in an ultrahigh-vacuum reaction chamber. The QMS was installed in a differentially pumped detection chamber to minimize background noise. The D flux at the surface was estimated from the D uptake curve measured on a Si(1 0 0) surface, where the sticking probability of D is widely accepted to be unity. The data showed the D flux to be $3.4 \pm 1.5 \times 10^{13}$ cm^{-2} s^{-1}. The base pressure of the reaction and detection chambers was 4×10^{-10} Torr after baking for 10 h at 150 °C.

3. Results and discussion

Ru films were oxidized by exposure to O atoms, and XPS spectra were taken by the procedure mentioned above. Fig. 1 shows O (1s) and Ru (3d) XPS spectra for various O exposure times. A small O (1s) peak was present even before O exposure (Fig. 1(a)); this is attributable to the O atoms in the native oxide on the surface. As the O dose increased, or in other words, as the exposure time increased from 1 to 30 min, the O (1s) peak became higher and broader, as can be seen in Fig. 1(b)–(d), which shows results obtained for exposure times of 1, 10, and 30 min. The corresponding Ru (3d) peaks shown on the right-hand side of Fig. 1 are basically composed of two spin-orbit components attributable to Ru ($3d_{5/2}$) and Ru ($3d_{3/2}$), which have peaks at around 280 and 284 eV, respectively. As the O exposure time increases, the bulk Ru (3d) peak decreases in intensity, while the chemically shifted components make the peak broader.

In order to find out how Ru films are oxidized by O atoms, we analyzed the XPS spectra for O (1s) and Ru (3d) by decomposing them into chemically shifted components. As mentioned before, the Ru films used were already naturally oxidized (Fig. 1(a)). The O (1s) spectrum for the naturally oxidized surface can be broken down into two components: one (green line) has a peak maximum at 530 eV, and the other (purple line) has a peak maximum at 531.5 eV. The corresponding Ru (3d) spectrum (Fig. 1(a)) measured before O exposure can also be decomposed into two components, in addition to the bulk one. The black line, for which the peak maximum is at 280 eV, represents bulk Ru atoms that have escaped oxidation. The red and blue lines, which have maxima at 280.5 and 281.6 eV, respectively, are related to Ru atoms bonded to O atoms, and correspond to the two O (1s) peaks in Fig. 1(a).

After a 1-min exposure to O atoms, the height of the O (1s) peak increased, while that of the Ru (3d) peak decreased, as shown in Fig. 1(b). Decomposition of the O (1s) and Ru (3d) spectra revealed the same spectral components as those in Fig. 1(a). Both the 530-eV O (1s) component and the 281.6-eV Ru (3d) component markedly increased in intensity, suggesting that they are due to the same Ru suboxides in the bulk layer. In contrast, the 531.5-eV O (1s) peak (purple line) did not measurably increase, which suggests that it is due to oxygen atoms that have adsorbed to the topmost Ru surface layer. These spectral assignments are in accordance with recent reports that Ru suboxides have a maximum Ru (3d) peak at around