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Atomic O and H exposure of C-covered and oxidized d-metal surfaces

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ABSTRACT

Carbon coverage, oxidation and reduction of Au, Pt, Pd, Rh, Cu, Ru, Ni and Co layers of 1.5 nm thickness on Mo have been characterized with ARPES and desorption spectroscopy upon exposure to thermal H and O radicals. We observe that only part of the carbon species is chemically eroded by atomic H exposure, yielding hydrocarbon desorption. Exposure to atomic O yields complete carbon erosion and CO_2 and H_2O desorption. A dramatic increase in metallic and non-metallic oxide is observed for especially Ni and Co surfaces, while for Au and Cu, the sub-surface Mo layer is much more oxidized. Although volatile oxides exist for some of the d-metals, there is no indication of d-metal erosion. Subsequent atomic H exposure reduces the clean oxides to a metallic state under desorption of H_2O. Due to its adequacy, we propose the atomic oxygen and subsequent atomic hydrogen sequence as a candidate for contamination removal in practical applications like photolithography at 13.5 nm radiation.

1. Introduction

In previous work we presented a study on the growth of thin d-metal surface layers with different oxidation, interface, and surface enthalpies [1] in a range of thicknesses onto Mo [2] and B_4C [3,4]. Both in ambient conditions and during intense illumination in vacuum, background C_xH_y and H_2O has been observed to adsorb and dissociate on the surface [5–8], resulting in condensed carbonaceous and oxide contaminants at the nanolayer surface [9–11]. Atomic hydrogen exposure (AHE) [12–15] and atomic oxygen exposure (AOE) [16,17] are two viable options to selectively remove these contaminants, respectively via rehydrogenation, or via oxidation to volatile molecules. AHE has been reported to produce both metal and semiconductor surfaces entirely free of contamination [18]. It can chemically erode contaminants such as oxygen on silicon and carbon on GaAs [19,20]. The arsenic and gallium oxides are reduced to volatile species of elemental arsenic, gallium oxide, gallium hydroxide and water, while LEED indicates good preservation of stoichiometry and surface order [21,22]. AOE yields an aggressive oxidation process that can mimic photo oxidation under high illumination fluxes. We use desorption spectroscopy and angular resolved X-ray photoelectron spectroscopy (ARPES) to investigate the potential of AHE and AOE. With the study of subsequent AOE and AHE, we also explore the feasibility of complete and faster contaminant erosion and recovering the surface to a metallic state. AHE and AOE are readily adaptable to in situ use in ultrahigh vacuum. Applications exist in a range of nano-devices and e.g. reflective multilayer optics for astronomy, medicine, and Extreme UV lithography (EUVL).

2. Experimental details

All investigated nanolayer surfaces or "caps" have been grown onto a Mo-on-Si layer on natively oxidized super polished Si substrates with ~0.1 nm rms roughness in an UHV electron beam evaporation coater with a base pressure of 1×10^{-6} Pa [23]. Growth rates in this particular work are 0.05 nm/s for Si, 0.04 nm/s for Mo, and 0.01 nm/s for the other d-metals. The deposited material mass is monitored by quartz crystal oscillator microbalances, which is recalculated to targeted homogeneous cap thickness equivalents of 1.5 nm for all materials. In case of closed layer-by-layer growth, the Mo layer is then protected from oxidation and the average ARPES intensity is optimal for identification [1,24,25]. Mentioned thicknesses are only an indication for the material quantity or average layer thickness, as several of the investigated d-metals are observed not to grow homogeneously onto Mo.

After deposition, the samples are stored in ambient conditions for saturation with oxide and hydrocarbon species of the multilayer surface. This is also the state in which they will be mounted for application as optical elements. The samples are as such introduced into an exposure chamber with a base pressure of 1×10^{-6} Pa for 1 h 1.0 sccm AHE to hydrogenate the condensed carbonaceous contamination to volatile species that desorb from the surface. Subsequently, 30 min 0.5 sccm AOE is applied which should oxidize the remaining C contamination to volatile carbon oxides. To reduce the resulting clean metal oxide surface, AHE is

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repeated. The H_2 and O_2 are catalytically dissociated in a water cooled Oxford Applied Research TC50 thermal cracking source that produces no ions [26,27]. It is directed at the sample surface at ~70 mm distance at a 45° angle. During AHE and AOE, the multilayer surface temperature does not exceed 358 K and 351 K, respectively. The pressure during treatment is 3.5×10^{-3} Pa, the desorbing fragments were monitored with a Prisma QMS 200 mass spectrometer.

In-depth distribution, compound formation, and chemical states before and after subsequent AHE and AOE were characterized with ARPES in a Thermo Theta Probe [1]. The setup is equipped with a field emission gun for secondary electron microscopy (SEM) and scanning Auger electron spectromicroscopy (SAM). SAM was implemented to provide increased lateral resolution in particular cases. Low energy ion scattering (LEIS) measurements have been performed at Calypso in Eindhoven, The Netherlands, to quantify surface monolayer composition and coverage in particular cases [28].

3. Results and discussion

As a reference for Mo oxidation, a 2.5 nm Mo layer on a 5.0 nm Si layer is deposited, without any protective capping layer. With ARPES we determined that approximately 30% of the Mo oxidizes to a MoO_3 film of ~0.6 nm thickness under ambient conditions for several weeks [1]. The oxide is however not self-terminating and oxidation continues until only MoO_3 is visible by ARPES. This process also occurs under EUV exposure in lithography tool vacuum due to physisorbed H_2O dissociation by secondary electrons [12]. The MoO_3 is reduced to Mo at the surface to within ~0.5 nm depth and to MoO_2 at the subsurface below upon AHE. The observation of surface Mo and subsurface MoO_2 suggests a two step process, where only direct interaction of H radicals with MoO_3 completely reduces it to Mo. This could then induce oxide segregation and $Mo + 2MoO_3 \rightarrow 3MoO_2$, leaving subsurface MoO_2 unreachable for direct interaction with H radials. The Mo is again completely oxidized to MoO_3 by AOE, but it can be recovered to the pre-AOE state by repeating the AHE. Since the oxidation of Mo yields layer degradation due to swelling, and cannot be fully recovered by AHE, the Mo surface should be capped by a separate capping layer with more appropriate process stability.

With a deposited equivalent of a 1.5 nm thick Au capping layer, selected as a first candidate capping material, the major fraction of the Mo is oxidized to MoO_3, with a $Mo3d_{5/2}$ peak appearing at 232.7 eV binding energy (BE) with a full width half maximum (FWHM) of 1.2 eV (Fig. 1). The O1s peak appears at 530.7 eV BE with 1.5 eV FWHM. The largely promoted oxidation, compared to bare Mo, can be attributed to earlier observed Au island growth on Mo due to an endothermic $\Delta H^{interface}$, resulting in high surface roughness and sacrificial functionality of the Mo [1,29]. The shape and position of the single Au4f doublet line of $Au4f_{7/5}$ at 83.9 eV BE and with 0.9 eV bandwidth at FWHM indicates that Au is not oxidized. Modeling of a C1s peak at 284.4 eV BE which dominates at grazing detection angles, indicates that the surface is covered by averagely 0.7 nm thick layer of C with mainly sp^2 hybridization. It is chemically viable that C preferentially resides at Au instead of MoO_3. AHE reduces all MoO_3 to MoO_2 and Mo in a 3:5 ratio, while the C content is some 55% lower. Observed CH_4 and H_2O desorption during AHE confirm hydrogenation of C and reduction of MoO_3.

During subsequent AOE, CO_2 desorption is observed, indicating oxidation and erosion of remaining carbonaceous contamination. ARPES reveals no C and no elemental Mo beside the MoO_3, while the Au remains entirely metallic. AHE reduces all MoO_3 to MoO_2 and Mo (Fig. 1).

With a 1.5 nm thick Pt cap layer, selected next, 10% of the Mo is oxidized to MoO_3, which appears to be intermixed with the Pt. The surface is covered by a 0.8 nm thick C layer. AHE erodes half of the C and most of the O content. Subsequent AOE erodes all C and dramatically increases the O content, although only some 20% of the Mo is oxidized to MoO_3. A second Pt4f doublet is detected for grazing angles with $Pt4f_{7/2}$ at 73.4 eV BE and ~1.5 eV bandwidth, suggesting 10% of the Pt is oxidized to PtO or Pt_3O_4 (Fig. 2). We observe no fragments that would suggest erosion by formation of volatile PtO_2. With AHE, the surface is reduced to pre-AOE state.

A 1.5 nm thick Pd capping layer allows for 60% of the Mo to oxidize to MoO_3, a ~0.3 nm thick PdO_2, a ~0.8 nm thick C overlayer and a CO monolayer. AHE reduces all PdO_2 and MoO_3 to its elemental state and erodes all CO, but leaves some carbonaceous contamination. AOE erodes this and oxidizes about 70% of the Pd to only PdO, with no visible PdO_2 (Fig. 3). Mo oxidizes for 20% to MoO_3, mainly located at the surface. No oxide remains after AHE.

A 1.5 nm thick Rh capping layer oxidizes for 20% to Rh_2O_3 with a ~0.8 nm thick C overlayer. Within the XPS detection range, no Mo but only MoO_3 is visible (Fig. 4). Both RhO and RhO_2 are volatile and would thus not occur in XPS. As these oxides have a positive formation enthalpy [29], formation is unlikely under ambient conditions, but possible in more aggressive environments. AHE results in reduction to MoO_2 (Fig. 4) and Rh, while most C remains. During AOE, we observe no fragments that could indicate Rh erosion via RhO or RhO_2 formation. The AOE does erode the remaining C, it oxidizes 55% of the Rh to Rh_2O_3 and all Mo to MoO_3. Upon subsequent AHE, the Rh_2O_3 and MoO_3 are fully reduced to their elemental state by AHE.

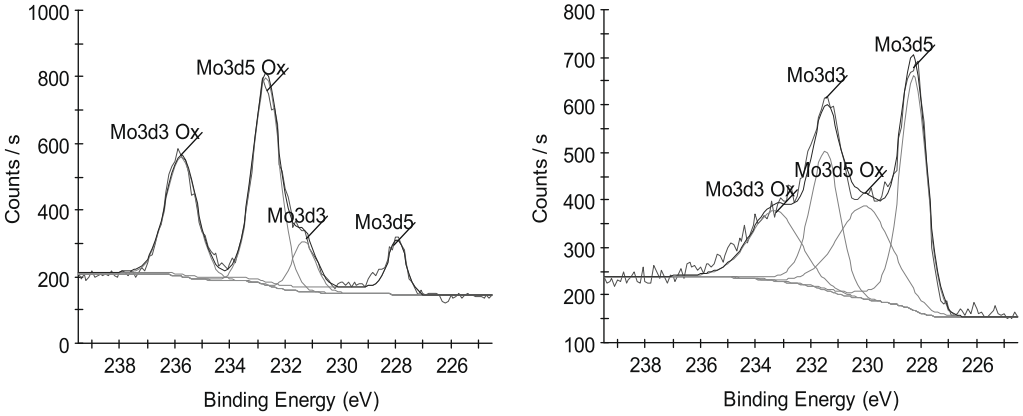

Fig. 1. Au cap: the Mo3d peaks before (left) and after (right) treatment sequence. All MoO_3 after AOE is reduced to MoO_2 and Mo by AHE.