Chemically mediated diffusion of d-metals and B through Si and agglomeration at Si-on-Mo interfaces

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Chemical diffusion and interlayer formation in thin layers and at interfaces is of increasing influence in nanoscopic devices, such as nanoelectronics and reflective multilayer optics. Chemical diffusion and agglomeration at interfaces of thin Ru, Mo, Si, and B4C layers have been studied with x-ray photoelectron spectroscopy, cross section electron energy loss spectroscopy, high-angle annular dark field scanning transmission electron microscopy, and energy dispersive x-ray in relation to observations in Ru-on-B4C capped Mo/Si multilayers. Rather than in the midst of the Si layer, silicides and borides are formed at the Si-on-Mo interface front, notably RuSi2 and MoBx. The interface apparently acts as a precursor for further chemical diffusion and agglomeration of B, Ru, and also other investigated d-metals. Reversed “substrate-on-adlayer” interfaces can yield entirely suppressed reactivity and diffusion, stressing the influence of surface free energy and the supply of atoms to the interface via segregation during thin layer growth. © 2009 American Institute of Physics. [DOI: 10.1063/1.3126497]

I. INTRODUCTION

The morphology of layer growth on a dissimilar substrate layer is affected by the lattice mismatch, the chemical reactivity, and the surface free energy difference.1,2 In this paper we characterize the influence of these factors by considering nanometer thin Ru, Mo, Si, and B4C substrate and adsorbate layers to cover a wide range of interface characteristics. Ru does not readily react with Mo and the two transition metals have comparable lattice spacings and surface free energies that are very different from Si and B4C. Mo forms a relatively stable silicide interface with Si,3 while Ru and some other d-metals diffuse into a Si substrate layer without significant reactivity.4 B4C dissociates upon deposition and readily forms borides with Mo and Ru, while carbides are only kinetically favored with Mo and Si.3 All materials involved are considered both as ad- and substrate layer to study the effect of dissociative B4C deposition as observed by Nedelcu et al.,3 and the surface free energy driven intermixture (segregation) on the adsorbate/substrate dependency for compound formation. Layer and interface growth and compound formation can be optically studied in multilayer coatings that act as artificial Bragg crystals. Reflective multilayer x-ray optics are also of increasing importance for applications in astronomy, medicine, and next generation lithography.

For extreme UV lithography (EUVL) (λ=13.5 nm), high contrast Mo/Si multilayers with individual layer thicknesses of 3–4 nm are applied as condenser, illuminator, and projection optics. To protect the reflecting mirror surface against photo induced oxidation and the resulting decrease in reflectivity, a capping layer is applied on top of the multilayer,5 with Ru as a common reference material.6,7 Cap thickness and intermixture with the layers beneath strongly influence the overall reflection and the protection that the cap offers. We relate our characterization of the interlayers between B4C, Ru, Mo, and Si to the application of a B4C diffusion barrier layer between the Ru and subsurface Si. This could reduce the overall intermixing and limit subsequent reflection loss, as proposed by Bájt et al.7

II. EXPERIMENTAL DETAILS

The layers have been grown onto natively oxidized super polished Si (100) substrates that are precoated with Si in an electron-beam physical vapor deposition setup with a base pressure of 1×10−6 Pa.8 This deposition technique was used for Si, B4C, Mo, and Ru to limit direct implantation of high energy atoms that might occur using higher adatom energy deposition techniques such as magnetron sputtering. Quartz crystal oscillator mass balances and in situ C Kα x-ray reflectometry are used for layer thickness control. A flux-shaping mask is used to deposit the B4C diffusion barrier with a lateral layer thickness gradient from 0.4 to 5.0 nm,9,10 before depositing the Ru capping layer.

A Thermo Theta Probe monochromated Al Kα x-ray photoelectron spectroscopy (XPS) setup with ion gun was used for sputtering and immediate subsequent on spot analysis of the in-depth material distribution and compound formation. The penetration and possible ion mixing depths of the used 0.5 keV Ar+ sputter ions at 45° incidence are ~1.6 nm in Si, ~1.3 nm in B4C, and ~0.7 nm in d-metals such as Mo and Ru.11 Considering the ~0.7 nm inelastic mean free path of the photoelectrons,12 the calculated ion mixing components are minor to moderate.

Differences in sputter efficiency and electron escape depths for the different materials result in underestimation of the Si content in the multilayer. This can result in early detection of subsurface elements during depth profiling, i.e., an apparent layer front shift to the surface. Thin layer systems

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thus appear more smeared out than they are. Considering that the XPS probing depth is considerably larger than the range of ion-beam induced chemistry, the in-depth modulation of electron binding energies, i.e., XPS peak shifts, can give a good indication of in-depth chemical states.

The depth scale in the graphs shown in this study is determined from the deposited layer thicknesses and periodicity in the multilayer as established by quartz microbalances and *in situ* reflection measurements. Differences in sputter efficiency and electron escape depths for the different materials that result in underestimation of the Si content in the multilayer are not of influence in the presented results, considering our focus on the surface composition and not on multilayer periodicity.

Cross section electron energy loss spectroscopy (CSEELS), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive x-ray (EDX) analysis were performed with a FEI Tecnai F30ST, operated at 300 kV. The samples were prepared by focused ion beam (FIB) using a FIB2000. This procedure damages the upper ~20 nm of the sample. The sample is first analyzed with a sample thickness of ~100 nm and ion-beam damage on both sides. Further thinning to <80 nm was achieved with low-energy ions.

**III. RESULTS AND DISCUSSION**

Figure 1 shows the sputter depth profiles of three Ru/B₄C/Si/Mo/Si multilayers with B₄C layer thicknesses of 5.0 nm (solid line), 1.7 nm (dashed line), and 0.4 nm (dotted line). The Ru and Si layers are kept at constant 1.5 and 2.5 nm thicknesses, respectively. The profiles are matched to the multilayer periods, with the top Si-on-Mo interface defined at 0 nm depth. Within the investigated range of B₄C barrier thicknesses, none of the B₄C diffusion barriers is observed to completely inhibit Ru diffusion. The increasing Ru residue below the B₄C layer for decreasing B₄C layer thickness has been confirmed using Auger electron spectroscopy depth profiling. Ru, Rh, Y, Nb, and Ir also diffuse through a Mo and Si layer to agglomerate at the Si-on-Mo interface, generalizing the observations for a range of *d*-metals. To verify that the observations are not a result of lateral Ru-on-B₄C growth inhomogeneity, Fig. 3 shows an atomic force microscopy (AFM) image of a Ru/B₄C capped multilayer surface when a 2.0 nm thick B₄C diffusion barrier is applied.

The AFM image in Fig. 3 reveals a 0.1 nm rms and 0.57 nm peak-to-valley roughness, indicating that Ru-on-B₄C growth and the observed diffusion do not increase roughness.
compared to Ru/Mo/Si/(Mo/Si) multilayers, for which Ru agglomeration at the Si-on-Mo interface front was also visible in 0.5 and 0.25 keV Ar⁺ depth profiles. The Ru agglomeration persisted or even increased after 48 h anneal at 300 °C, implying that the agglomeration is a thermodynamically preferred configuration.

Figure 4 shows the Ru 3d_{5/2} in-depth peak shift from its elemental value in reference to the Fermi level, giving an indication of the chemical state and compound formation. The in-depth Ru 3d_{5/2} BE modulation up to 0.5 eV in the 4.3 and 5.0 nm thick B₄C layers cannot be attributed to oxidation as is the case at the surface, since no subsurface oxygen is observed in XPS. A coinciding C 1s BE increase from 284.5 eV to 288.6 eV suggests RuB formation at the cost of B₄C decomposition. The C 1s peak appears to shift from 282.0 to 282.8 eV, suggesting a transition from carbide (B₄C) in the direction of the elemental value of 284.5 eV. Toward the Si/Mo interface, the Si 2p BE increase in 0.3 eV suggests silicide formation. The Mo 3d_{5/2} peak at 227.8 eV BE excludes neither elemental Mo nor a silicide. At the Si/Mo interface, the decrease in Ru 3d_{5/2} BE observed in Fig. 4 suggests Ru₂Si₃ formation. This means that the Ru agglomeration, as observed in Fig. 2, coincides and likely is a result of Ru₂Si₃ formation at the Si/Mo interface, which would sustain Ru migration. Toward the Si/Mo interface, a change in the nearest neighbor distance and/or formation of Mo silicides could accommodate Ru₂Si₃ formation. With $E_{\text{act}} = 130$ kJ/mol, MoSi₂ could be an intermediate or precursor for Ru₂Si₃ formation, for which $E_{\text{act}} = 174$ kJ/mol. Ronay and Schad observed similar precursor functionality of Cu₃Si, which was found to lower the formation temperature of ReSi₂. Like Ru, B is observed to agglomerate at the Si/Mo interface, as can be seen in Fig. 5.

The B tail in Fig. 5 shows a similar slope for the various B₄C layer thicknesses systems. Small differences can be attributed to ion mixing which is more prominent when more B₄C is present in the system. The B agglomeration is accompanied by a significant B 1s electron BE increase in the Mo layer, suggesting that B migration toward the Mo layer isaccompanied by MoBₓ formation, which stops further B diffusion. A similar mechanism occurs in the multilayer when B₄C diffusion barriers are applied. Figure 6 shows a ~0.3 nm beam size EELS cross section of a multilayer with five periods of 3.5 nm thick Mo and Si layers on five periods of 3.0 nm thick Mo and Si layers with a 1.0 nm thick B₄C barrier at each interface. The profiles are corrected for the total transmission of the TEM sample, which is much less in Mo than in Si.

The CS-EELS in Fig. 6 reveals highly localized B peaks that are predominantly located in the Mo layers. This means that the B diffuses from both the Mo/Si and Si/Mo interface into the Mo layer, where it can form MoBₓ. The in-depth C distribution appears very diffusive with probably a large contribution from the sample preparation. The 16%–84% Mo-on-Si and Si-on-Mo interface widths are 1.08 and 1.24 nm, respectively, compared to 1.75 and 1.50 nm without B₄C. The difference at the Si-on-Mo interface is within the finite resolution and the instrumental error, but the Mo-on-Si interface profiles from reduced segregation by application of a B₄C diffusion barrier. HAADF-STEM and EDX analysis with a beam size of ~1.0 nm confirm the observations in Fig. 7, although the barrier layers are not individually identifiable.

In Fig. 7, the B and C presence also appear to reduce layer inhomogeneity and interface diffuseness. In XPS depth profiling studies on Si/Mo multilayers with B₄C diffusion...
barriers, we observe a locally B-rich stoichiometry, while C is more diffused. In the case of Si and B₄C, borides will not spontaneously form due to unfavorable formation enthalpy. Only elemental C that is in equilibrium with B₄C can react spontaneously form due to unfavorable formation enthalpy. This implies formation of RuB via Eq. 2. 

$$K = e^{-\Delta G_{for}/RT} = e^{\Delta G_{for}/RT} = e^{-\Delta H_{for}/RT},$$

where the $\Delta G_{for}$ term covers differences in phase and crystal structure. Since these differences are small for solid-solid interactions occurring at the interface, we take $\Delta G_{for} = \Delta H_{for}$.

Mo₂C deposition onto Si results in a chemically in-active interface with significant B₄C segregation toward the subsurface to maintain a surface monolayer of Si, of which both the surface free energy and the enthalpy for vacancy formation are lowest.

When B₄C is atomically deposited onto Ru or Mo, the largest kinetic gain is obtained, respectively, by

$$4Ru + 4B + C \rightarrow 4RuB + C,$$

and

$$6Mo + 4B + C \rightarrow 4MoB + Mo_2C,$$

with $\Delta H_{for}^{RuB} = -35 \text{ kJ/mol}$, $\Delta H_{for}^{Mo_2C} = -62 \text{ kJ/mol}$, $\Delta H_{for}^{Mo_2C} = -46 \text{ kJ/mol}$, and negligible Ru and Mo lattice energy.

The experimental results show reactive interfaces when B₄C is used in multilayer applications. Increased B concentration and B 1s electron BE at the B₄C/Mo interface hint at MoB formation via Eq. (3). Transition metal boride and carbide formation at B₄C interfaces has also been observed by Mogilevsky et al. In the experiments, various metal borides and carbides appear to be favored over B₄C, in accordance with the earlier described thermodynamics. To identify the adsorbate/substrate dependency of thin layer growth mecha-

FIG. 7. Cross section EDX (left) and high resolution (<0.3 nm) HAADF-STEM (right) image of a Ru capped 5 × (Mo/Si) 5 × (Mo/B₄C/Si/B₄C) multilayer.

nisms, Fig. 8 shows an XPS sputter depth profile of a four material multilayer with interfaces in all the possible orientations: Si/Ru/Mo/B₄C/Si/Mo/Ru/B₄C/Mo/Si/B₄C/Ru/Si. Ru and Mo layers are 4 nm thick, first and last Si layer is 7 nm, B₄C and other two Si layers is 15 nm.

From the depth profile, it is clear that the sputter rate for B₄C is significantly lower than for Si. Si segregation into B₄C is again visible for B₄C on Si, and to lesser extends for B₄C on Ru and B₄C on Mo, indicating a moderately high surface free energy of the deposited B₄C. Like Ru, diffusion of Mo into a B₄C substrate layer is significant. Clear Mo segregation into Si and relatively sharp B₄C/Mo and Si/Mo interfaces are also visible. For in-depth chemical analysis, Fig. 9 shows the B 1s, C 1s, Ru 3d, Mo 3d, and Si 2p peak shifts from bulk values, superimposed on the depth profile.

Segregation of Mo, similar to Ru, delays B₄C depletion and results in a broad MoB and Mo₂C interlayer. Si 2p, Mo 3d, and Ru 3d electrons all show a considerable upward BE shift when the corresponding materials are deposited onto B₄C, while the shift is much smaller when these materials form the substrate layer for B₄C growth. Significant

FIG. 8. XPS sputter depth profile of a four material multilayer system with all ad-/substrate layer combinations. B bonded to C is denoted B (c).

FIG. 9. (Color online) Peak-shifts (dots, superimposed on the depth profile) for Ru 3d, C 1s, B 1s, Si 2p, and Mo 3d as determined by XPS sputter depth profiling. A 0.0 eV peak shift represents binding energies of 280.0, 283.0, 188.0, 99.3, and 227.8 eV for the respective materials.
B 1s peak shifts are observed for B₄C interfaces with Mo and Ru. When Ru is replaced by Y, which has the lowest surface free energy per unit area of the d-metals, we observe quite similar diffusion and compound formation. It is remarkable that the BE shifts appear much more adsorbate/substrate than material dependent and that instead of B₄C dissociation, the supply of atoms via segregation is of main influence.

IV. CONCLUSION

Diffusion and compound formation in Ru, Mo, Si, and B₄C layers have been characterized with XPS, CS-EELS, HAADF-STEM, and EDX. Minimization of the surface free energy causes significant B₄C surface segregation into the Si, driving Si toward the surface. The intermixture is not accompanied by chemical activity. The B 1s, C 1s, and Si 2p electron binding energies reveal no SiB and SiC, both species not being kinetically favored over B₄C.

Significant Ru surface segregation and further diffusion into the B₄C and Si layer occur for all B₄C diffusion barrier thicknesses up to 5.0 nm. Ru diffusion coincides with Ru 3d, B 1s, and C 1s electron binding energies that suggest Ru boride formation at the cost of B₄C, particularly for the thickest B₄C layers.

Ru and B diffuse through the Si layer toward the Si/Mo interface front, where agglomeration occurs. This is in accordance with earlier experimental results, which showed Ru agglomeration to also be persistent after annealing. Shifts in the Ru 3d and B 1s electron binding energies suggest the agglomeration is accompanied by Ru₂Si₃ and MoB formation. Our results confirm earlier conclusions that the Si/Mo interface front acts as a precursor for Ru silicide formation, accommodating Ru migration to minimize the energy. The observations for Ru can be generalized to other d-metals including Y, Nb, Rh, and Ir. B agglomeration is found to be accompanied by MoB formation, which is strongly favored over the endothermic SiB formation process and to a lesser extent over formation of RuB.

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