Introduction

The Si₃N₄/TiN Interface: An Introduction to a Series of Ultrathin Films Grown and Analyzed *In situ* using X-ray Photoelectron Spectroscopy

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Superhard nanostructured materials, such as nanocomposites and nanolaminates, are subjects of intense interest in materials research. The bulk properties of these materials are often defined by the physical and electronic structure of internal interfaces, which are not well understood. The nanocomposites consist of crystallites (≤ 10 nm) of transition metal nitrides, carbides or borides encapsulated by a few monolayers (ML) of a covalent tissue phase (e.g., Si₃N₄, BN, CN_x, or C). Due to the small dimensions of these nanostructures, nucleation and propagation of dislocations is impeded, while the high cohesive strength of the intergranular tissue layer inhibits grain-boundary sliding (Ref. 1). The nature of the bonding between the crystallite and tissue phases is an important determinant factor defining the macroscopic properties of these materials. An example of a superhard nanocomposite which has served as a model system is TiN/Si₃N₄.

The chemical nature of the SiN_x/TiN interface can, in principle, be examined using angle-resolved X-ray photoelectron spectroscopy (AR-XPS). In practice, however, these nanocomposite are three-dimensional with interfacial layers possessing a high curvature. Here, a series of planar bilayers, with 4-ML-thick overlayers, were deposited *in situ* by ultrahigh vacuum magnetron sputter deposition onto epitaxial TiN/MgO(001) in order to probe the electronic structure of Si₃N₄/TiN(001), Si/TiN(001), and Ti/Ti(001) interfaces using angle-resolved X-ray photoelectron spectroscopy (Ref. 2). The 4-ML-overlayer thickness is similar to reported values for the tissue phase and is also electron-transparent. To minimize the effects of contamination, the growth experiments were performed in a multichamber ultrahigh vacuum (UHV) system and analyzed *in situ* following direct vacuum transfer from the growth chamber to the spectrometer.

The Ti 2p photoelectron spectra of clean TiN, shown in Figure 1, are characterized by 2p_{3/2} and 2p_{1/2} lines appearing at 454.7 and 460.7 eV, each with corresponding satellite lines which are shifted ~ 2.6 eV to higher binding energies. There is no discernible relationship between the intensities of the satellites and the photoelectron emission angle. The satellites are intrinsic to the photoelectron line-

shape of TiN and are very sensitive to the chemical/electronic environment around the Ti atoms (Ref. 3). Porte *et al.* (Ref. 4) observed that the intensity of the satellites varied with the sample N/Ti ratio in the range from 0.52 to 0.97, with the higher N/Ti ratio samples having the more intense satellite intensity. Furthermore, when the surface of stoichiometric TiN is subject to Ar⁺ ion bombardment, under conditions typical for sample cleaning, the intensities of the satellite features decrease to nearly zero due to the preferential removal of N (Ref. 5). The intensity of the satellite peaks can be restored by bombarding the sputtered surface with 2.4 keV N₂⁺ ions (Ref. 6).

Two models have been proposed to explain the TiN Ti 2p satellite peaks. The first describes the satellites as being due to core hole screening related to vacancy defect states (Ref. 7), while the other attributes them to plasmon loss features (collective oscillation modes of conduction band electrons) giving rise to an energy loss $\hbar\omega \sim 2.6$ eV (Ref. 8 and 9). If the satellites were entirely the result of plasmon energy loss, one would expect to observe satellite features of similar intensities for other photoelectron lines, such as N 1s, as well. Additional higher-order satellites occurring at $2\hbar\omega$ should also be seen. The N1s spectrum of TiN instead shows a satellite feature much lower in intensity than those observed in the Ti 2p spectrum with an energy difference of 2.5 eV which we do attribute to a plasmon loss (Refs. 3 and 8). Thus, it is concluded that the majority of the intensity in the Ti 2p satellite features is related to core hole screening with a minor contribution resulting from a plasmon energy loss.

Ionization of the 2p core subshell results in a strong coulombic perturbation producing localized exciton-like states (Ref. 10). Final-state screening occurs when there is localization of electron density around the core-ionized atoms (Ref. 11). When electron density is not directed towards these localized states, unscreened final states are created. In certain cases, the core-ionized atoms relax producing both screened and unscreened final states. When this is the case, the photoelectron spectrum will include features due to both screened and unscreened final states, as the spectrum represents the final state configuration of the core-ionized atoms.

Incomplete core hole screening will result in the appearance of spectral features at higher binding energies due to a stronger interaction between the core-electron and the nucleus. This suggests that the satellite feature represents unscreened final states.

Figure 2 compares the Ti 2p photoelectron spectrum of TiN(001) to the photoelectron spectra of Si₃N₄/TiN(001) bilayers for which Si₃N₄ is deposited at three different substrate biases. The Ti 2p spectra show that the intensity of the Ti 2p satellite features dramatically increases, even for the lowest bias samples, -7 V. Furthermore, when the substrate bias during deposition is increased, the satellite Ti 2p intensities increase as well to the point at which the intensity of the satellite line for Si₃N₄/TiN(001) samples grown with a -250 V bias is nearly as intense as the Ti 2p_{3/2} line. According to the model described by Egelhoff (11), an increase in the intensity of the unscreened final states suggests a polarization of electron density at the interface away from TiN toward Si₃N₄, with less electron density available to screen the Ti 2p core hole.

In order to understand the effect of the degree of nitridation on the electronic structure of the Si₃N₄/TiN interface, a comparison of the Ti 2p photoelectron spectrum of TiN(001) to the photoelectron spectra of Si/TiN(001) and Ti/TiN(001) layers is provided in Figure 3. When 4-ML Si layers are deposited onto TiN(001), the intensity of the unscreened final state features decrease. The unscreened final state features of 4-ML Ti layers on TiN(001) are diminished even further to the point at which the Ti 2p spectrum resembles that obtained from Ti. In each case, the nitrogen-deficient Si/TiN(001) and Ti/TiN(001) interfaces have increased electron density available to screen the Ti 2p core hole as compared to the Si₃N₄/TiN(001) bilayer system.

Transfer of electron density from TiN toward the TiN/Si₃N₄ interface can provide a partial explanation of the enhanced hardness of the Si₃N₄/TiN nanocomposite system compared to pure

TiN. The hardness of Si₃N₄/TiN nanocomposites is approximately 35 GPa (Ref. 12), while $H \sim 23$ GPa (Ref. 13) for pure polycrystalline TiN. SiN_x nanocomposites with $x=0.95$ exhibit no enhancement in hardness. The enhanced unscreened final state satellite intensities as shown in Figure 2 indicates interfacial electron density is directed towards the Si₃N₄ layers, whereas the diminished final state satellite intensities for the Si/TiN(001) and Ti/TiN(001) layers, shown in Figure 3, suggests that electron density is not directed from TiN toward the overlayers.

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FIG. 1 Angle-resolved Ti 2p photoelectron spectra acquired at emission angles of 0, 60, and 75 degrees from epitaxial TiN(001) grown *in situ*.

FIG. 2 Ti 2p photoelectron spectra acquired at a 75 degree emission angle from epitaxial TiN(001) grown *in situ* and $\text{Si}_3\text{N}_4/\text{TiN}(001)$ bilayers grown *in situ*. The Si_3N_4 overlayers were deposited with biases of -7 , -150 , and -250 V.

FIG. 3 Ti 2p photoelectron spectrum acquired at a 75 degree emission angle from epitaxial TiN(001) grown *in situ* and Ti 2p photoelectron spectra acquired at a 0 degree emission angle from Si/TiN(001) and Ti/TiN(001) bilayers grown *in situ*.