Nanostructure formation during deposition of TiN/Si$_3$N$_4$ nanomultilayer films by reactive dual magnetron sputtering

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Growth of multilayer or superlattice thin films has shown various degrees of hardness enhancements often exceeding the individual hardness of the materials involved. Typically the hardness increases with decreasing wavelength until a maximum value is reached in the nm range, after which the hardness decreases with further decrease in wavelength$^{1,2}$. Different theories have been developed in order to explain the observed increase in hardness. Koehler$^3$ showed theoretically a hardness increase for materials with a lamellar structure. This increase arises from image forces on dislocations due to a shear modulus difference between the layers. Other theories that tries to explain the observed increase in hardness are, coherency stress hardening$^{4-6}$, where dislocation movement is restricted by the stress fields present at coherent interfaces within the multilayer. Also, the epitaxial stabilization effect has been demonstrated$^7$, where a metastable structure for one of the layer materials is formed by pseudomorphic forces to the surface of the other layer during nucleation and growth thus creating a coherent interface, e.g., a normally amorphous material assuming crystalline structure for small layer thicknesses. For Orowan-like strengthening$^{8-11}$, plastic deformation occurs by dislocation movement and bowing inside layers. Finally, in the case of Hall-Petch strengthening$^{12,13}$ hardness increases due to a reduction in grain size and thereby an increase in grain boundary density, grain boundaries which acts as dislocation obstacles.

Multilayer thin films consisting of titanium nitride (TiN) and silicon nitride (Si$_3$N$_4$) layers with compositional modulation periodicities between 3.7 and 101.7 nm have been grown on silicon wafers using reactive magnetron sputtering. Electron microscopy and X-ray diffraction studies showed that the layering is flat with distinct interfaces. According to the XRD studies (figure 1), the deposited TiN layers were crystalline and exhibited a preferred 002 orientation for layer thicknesses of 4.5 nm and below. For larger TiN layer thicknesses, a mixed 111/002 preferred orientation was present as the competitive growth favored 111 texture in monolithic TiN films. The TEM studies (figure 2) revealed that the Si$_3$N$_4$ layers exhibited amorphous structure for layer thicknesses $\geq$ 0.8 nm, however, for the first time cubic crystalline silicon nitride phase was observed for layer thicknesses $\leq$ 0.3 nm. Formation of this metastable SiN$_x$ phase is explained by epitaxial stabilization to TiN. The microstructure of the multilayers displayed columnar growth within the TiN layers with intermittent TiN renucleation after each Si$_3$N$_4$ layer. A nano-brick-wall structure was thus demonstrated over a range of periodicities. As-deposited films exhibited relatively constant residual stress levels of 1.3±0.7 GPa (compressive) independent of the layering. Nanoindentation was used to determine the hardness of the films, and the measurements showed an increase in hardness for the multilayered films compared to the monolithic Si$_3$N$_4$ and TiN films, as shown in figure 3. The hardness results varied between 18 GPa for the monolithic TiN film, up to 32 GPa for the hardest multilayer, which corresponds to the presence of cubic SiN$_x$. For larger wavelengths, $\geq$20 nm, the observed hardness correlate to the layer thickness similar to a Hall-Petch dependence, but with a generalized power of 0.4. Sources to the hardness increase for shorter wavelengths are discussed, e.g. epitaxial stabilization of metastable cubic SiN$_x$, coherency stress, and impeded dislocation activity.

REFERENCES

Figure 1 (a) High angle XRD scan from a set of TiN/Si$_3$N$_4$ multilayer films with constant TiN layer thickness of 4.5 nm. (b) High angle XRD scan from the set of TiN/Si$_3$N$_4$ multilayers with constant Si$_3$N$_4$ layer thickness of 1.7 nm. A monolithic TiN film is added for reference.

Figure 2 XTEM micrograph and SAD patterns from TiN/Si$_3$N$_4$ multilayer samples with (a) periodicity 11.5 nm and Si$_3$N$_4$ layer thickness of 1.7 nm; (b) periodicity 4.8 nm and $l_{\text{SiN}} = 0.3$ nm and (c) layer thicknesses of 100 nm TiN and 1.7 nm Si$_3$N$_4$ respectively.

Figure 3 (a) Hardness values from the samples with constant Si$_3$N$_4$ layer thickness (1.7 nm) and (b) Hardness values from the samples with constant TiN layer thickness (4.5 nm).