Abstract

The Ni-TiN based nanocomposite thin films were deposited by reactive magnetron co-sputtering of high purity (≈99.999%) Ti and Ni targets used as RF and DC sources, respectively in Ar+N_2 atmosphere on silicon (100) substrate with different Ar:N_2 ratios (1:1, 1:2 and 1:3), negative substrate bias voltages (0 to –80 V) and substrate temperatures (ambient to 700 ^{o}C). The deposition rates obtained from thickness measurements (film thickness in the range of ≈350-500 nm) using a contact-type profilometer have been found to decrease with decrease in Ar:N_2 (increasing Ar content of gas mixture), and also with increase in negative substrate bias or temperature of substrate due to resputtering or desorption, respectively. On the other hand, the surface roughness measured by atomic force microscopy is found to be lowered with decreasing Ar:N_2 or increasing negative substrate bias up to -60 V. X-ray diffraction (XRD) analysis has shown the presence of Ni and TiN phases with preferred orientations of <111> and <100>, respectively, in the as-deposited films, which is known to lower their surface energies. However, for deposition at temperatures ≥500 ^{o}C, TiN<111> is preferred probably causing lowering of elastic strain energy. The results of X-ray photoelectron spectroscopy has shown TiN to be sub-stoichiometric, stoichiometric and over-stoichiometric in the films deposited at ambient temperature using Ar:N_2 = 1:1, 1:2 and 1:3, respectively, with the oxygen content being minimum for substrate bias of -60 V, and maximum for deposition at 700 ^{o}C. Based on these results, Ar:N_2 = 1:2 and substrate bias = -60 V have been considered as the optimum conditions for deposition of the nanocomposite films at ambient temperature. The volume fraction of TiN, as measured by Reitveld analysis of the XRD peaks, is found to increase from 22 to 44% with decrease in Ar:N_2 from 1:1 to 1:3, or from 36 to 50% with increase in negative substrate bias from 0 to -80 V.

Characterization of microstructures by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) has shown reduction in porosity content with reduction in film growth rate by decreasing either Ar:N_2 ratio or increasing negative substrate bias. Studies using both XRD and TEM have shown that grain sizes of Ni (range of ≈10-20 nm) and TiN (range of ≈6-9 nm) in the nanocomposite films are decreased with increase in either Ar:N_2 gas ratio or negative substrate bias. But in the nanocomposite thin films deposited at 500 °C and 700 °C, non-uniform grain growth with presence of pores has been observed, which in turn leads to enhanced surface roughness The stress in the films obtained by XRD based $\sin^2\Psi$ method is found to become more compressive with decrease in $Ar:N_2$ or increase in negative substrate bias. However, the magnitude of compressive residual stress is found to decrease with increase in substrate temperature used for deposition. The films deposited at ambient temperature and annealed at temperatures used for deposition show finer grain size, as well as lower roughness and stress compared to those of the corresponding as-deposited films.

Nanoindentation studies have shown hardness and elastic moduli of the nanocomposite films to rise linearly with increase in TiN content, and decrease with increase in substrate temperature $\geq 500\ ^{o}C$. Interestingly, the hardness values are found to exceed rule of mixture predictions, probably due to finer grain size, root mean square strain and image forces restricting dislocation motion. The scratch resistance is found to scale with resistance to plastic deformation, which is further justified by observation of ploughing as the operating wear mechanism. The coefficient of friction is found to be lower for the Ni-TiN nanocomposite films than that for Ni, probably due to higher roughness and increased adhesive wear of the latter film. Both hardness and elastic modulus are found to increase with growth temperature to 300 °C and then decrease due to the combined effect of intercolumnar porosity and grain growth. Electrical resistivity measured by Van der Pauw four-point probe method appears to be proportional to the TiN volume fraction. Studies of the electrochemical behavior of the film investigated using potentiodynamic polarization experiment in 3.5 g/l NaCl solution has shown sharp decrease in corrosion rate of Ni matrix with addition of TiN due to formation of passive film of TiO_2 on the surfaces. Furthermore, alloying of the Ni-matrix with 10 wt% Cu is found to further enhance mechanical properties and corrosion resistance, while lowering its electrical resistivity compared to those found for the Ni-TiN nanocomposite thin film grown under identical conditions.

Keywords: *Nanocomposite; Ni-TiN thin films, Reactive RF/DC magnetron sputtering; microstructure; stress; hardness; scratch; corrosion; resistivity*