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APPLIED PHYSICS LETTERS **86**, 161910 (2005)

Bonding properties and their relation to residual stress and refractive index of amorphous Ta(N,O) films investigated by x-ray absorption spectroscopy

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This work presents N, O *K*-edge x-ray absorption near-edge structure (XANES) and Ta L_3-edge extended x-ray absorption fine structure (EXAFS) studies of amorphous Ta(N,O) films prepared with various flow rate ratios of N_2/O_2. The N and O *K*-edge XANES and Ta L_3-edge EXAFS spectra demonstrate the presence of N_2 molecules. These spectra also show that Ta(N,O) films have similar local atomic structure as that of Ta_2O_5. No evidence of the formation of Ta–N bond was obtained. The intensities of the π^* feature in the N *K*-edge spectra and the features of O 2*p*–Ta 5*d* hybridized states were found to correlate with the residual stress and the refractive index, respectively. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1905784]

As the demand for superior performance, efficiency, speed, and smaller size of electronic devices increases, the microelectronic industry has adopted copper as the interconnect material in ultralarge scale integrated devices.[1–3] Copper with a lower electrical resistivity and high electromigration resistance outperforms aluminum as an interconnect material. However, Cu can easily form Cu–Si compounds with the Si substrate.[2,4] Thus, a barrier layer is required to prevent formation of Cu–Si compounds. Films of transition-metal (TM) nitrides are known to be good candidates for these purposes.[4–6] Among these nitrides, Ta-based compounds have attracted much interest in recent years because they have high thermal stability and do not react much with Cu.[3,6–8] One of the main difficulties encountered in barrier-layer applications is the diffusion of Cu through grain boundaries, which finally causes device failure. A solution to this problem is to add smaller atoms such as N, O, B, and P to TMs. Alternatively, films prepared in the amorphous form can also be used as barrier layers.[6] Ta(N,O) films, which are thermally stable and chemically inert toward Cu are promising as barrier material and can be prepared in the amorphous form.[6] Chang *et al.*[9] found that increasing the N_2 flow rate reduces grain sizes and increases the resistivity of TaN films. In earlier investigations,[10,11] Jong *et al.* prepared Ta(N,O) films in the amorphous form and examined their optical properties, residual stress, and microstructure. The bonding properties of Ta(N,O) films have received little attention and the roles played by N and O are unclear. Therefore, in this work, x-ray absorption studies of amorphous Ta(N,O) films are performed to elucidate their bonding properties.

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N and O *K*-edge x-ray absorption near edge spectra (XANES) and Ta L_3-edge extended x-ray absorption fine structure (EXAFS) measurements were performed at the National Synchrotron Radiation Research Center, in Hsinchu, Taiwan. All of these spectra were obtained by fluorescence yield method. Amorphous Ta(N,O) films were grown on a silicon substrate by rf sputtering by introducing N_2, O_2, and Ar gases simultaneously into the sputtering chamber. X-ray diffraction measurement indicated that these films are amorphous. Table I lists the N_2 and O_2 flow rates, N_2/O_2 flow rate ratio (ρ), N/O content ratio measured by Auger electron spectroscopy (AES), residual stress, and refractive index of these Ta(N,O) films. Details of the preparation and characterization of the Ta(N,O) films can be found elsewhere.[10,11]

Figure 1 presents the normalized N *K*-edge XANES spectra of Ta(N,O) and reference TaN films. A strong resonance peak at ~401.6 eV(A_1) and a broad feature centered at ~420 eV(B_1) were observed in the spectra. These features corresponds to N $1s \rightarrow 2p$ π^* and σ^* states, respectively.[12,13] Some very weak additional features were observed between π^* and σ^* features, which have been magnified ten times for clarity. These features are associated with transitions to Rydberg states and multielectron excitations.[13–15] The spectra of

TABLE I. Values of the N_2 and O_2 flow rates (f.r.) in the unit of sccm, N_2/O_2 flow rate ratio (ρ), N/O content ratio, residual stress and refractive index of Ta(N,O) films. The N/O content ratios were determined by AES.

Samples No.	N_2 f.r. (sccm)	O_2 f.r. (sccm)	ρ	N/O ratio	Residual stress ($\times 10^{-3}$ GPa)	Refractive index
N_1O_4	3	12	0.25	0.74	−5.0	2.03
N_1O_2	5	10	0.5	0.85	−8.0	1.98
N_1O_1	7.5	7.5	1.0	0.85	−7.5	2.12
N_2O_1	10	5	2.0	0.89	−6.5	2.08

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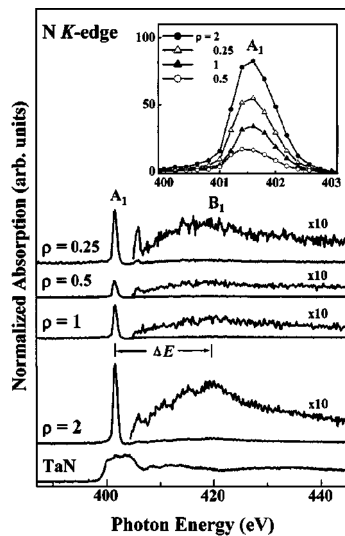

FIG. 1. Normalized N K-edge XANES spectra of Ta(N,O) films and reference TaN. The inset displays the π^* features.

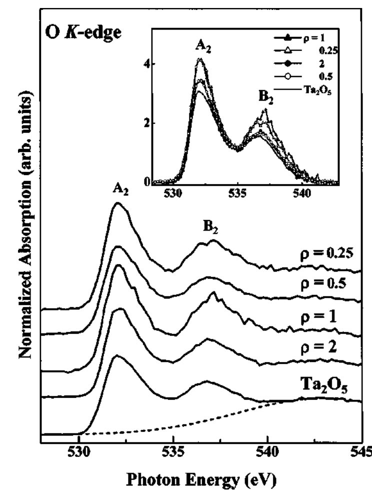

FIG. 2. O K-edge XANES spectra of Ta(N,O) films and Ta_2O_5 reference. The inset presents the A_2 and B_2 features with the background subtracted.

Ta(N,O) films differ substantially from that of the TaN reference sample as shown in the figure. In contrast, these spectra and the separation between π^* and σ^* features, ΔE, of $\sim$18.4 eV are very similar to those of the molecular nitrogen observed by Yagishita *et al.*[12] and Wenzel *et al.*[14] using XANES measurements. This result provides clear evidence for the presence of N_2 molecules and excludes the possibility of the formation of N–O nor N–Ta bonds in Ta(N,O) films because ΔE for N–O is 13.0 eV[12,15] and for N–Ta is 24.0 eV.[16] The bond strengths of N–N, N–Ta, O–O, and O–Ta diatomic molecules are 945.33, 611, 498.36, and 799.1 kJ/mol, respectively.[17] The N–N bond is much stronger than the N–Ta bond, which may be the reason for the presence of undissociated N_2 molecules. In contrast, O–Ta bond is much stronger than the O–O bond, so that Ta–O networks form readily. The inset of Fig. 1 plots π^* features for all Ta(N,O) samples. The intensity decreases initially as ρ is increased from 0.25 to 0.5 and then increases as ρ increases further from 0.5 to 2.0.

Figure 2 displays the normalized O K-edge XANES spectra of Ta(N,O) films and reference Ta_2O_5. These spectra exhibit two broad features, A_2 and B_2, which are separated by $\sim$4.7 eV with an intensity ratio near 3:2 for the Ta(N,O) films considered. These peaks correspond to transition of the O 1s core electron to unoccupied O 2p and Ta 5d crystal-field split t_{2g} and e_g hybridized states.[16,18,19] These spectra are nearly identical to that of the Ta_2O_5 reference sample with the same A_2–B_2 separation of $\sim$4.7 eV and intensity ratio of about 3:2. The O K-edge XANES spectra of many TM oxides with empty d band are very similar to those observed presently for Ta(N,O) films.[18,20] Figure 2 clearly demonstrates that the spectra of all Ta(N,O) samples are nearly identical to that of reference Ta_2O_5 suggesting that the local electronic structure of Ta atoms in Ta(N,O) samples is similar to that of Ta in Ta_2O_5. The intensities of A_2 and B_2 features, shown in the inset after a Gaussian background subtraction (dashed line) change with ρ, but not in a systematic manner.

Figure 3 plots the Fourier transform (FT) of EXAFS $k^3\chi$ data (as shown in the inset) at the Ta L_3 edge for all Ta(N,O) samples (where k ranges from 3.5 to 11 Å^{-1}) and reference samples, Ta_2O_5, TaN, and Ta metal. The main peaks, A_3–D_3, in these FT spectra are attributable to the nearest-neighbor (NN) Ta–O [in Ta(N,O) films and Ta_2O_5], Ta–N (in TaN), Ta–Ta (in Ta metal), and next-neighbor-neighbor (NNN) Ta–Ta (in TaN) bond lengths, respectively.[21,22] The NN Ta–O bond lengths in Ta(N,O) samples prepared with ρ=2.0, 1.0, 0.5, and 0.25 are essentially the same as indicated by the vertical dashed line. The Ta(N,O) FT spectra are similar to that of Ta_2O_5, while they are very different from those of TaN and Ta metal. Thus, present EXAFS results show that Ta(N,O) films lack NN Ta–N and NNN Ta–Ta bonds and essentially contain only Ta–O bonds with a local atomic structure similar to that of Ta_2O_5. This result is consistent with XANES measurements.

The x-ray absorption results presented above demonstrated that amorphous Ta(N,O) films contain mostly Ta–O bonds with a local environment similar to that of Ta_2O_5. The results also show presence of N_2 molecules, which most likely are located in the boundary regions between Ta–O domains/fragments. Figure 4(a) plots the integrated intensity within the energy range between 400.6 to 403.0 eV of the π^* feature in N K-edge XANES spectra (inset of Fig. 1) as a function of ρ. This figure also includes the residual stress in Ta(N,O) films listed in Table I. The π^* integrated intensity

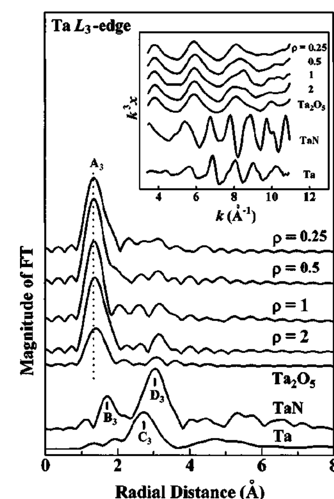

FIG. 3. Fourier transform spectra of the EXAFS $k^3\chi$ data at the Ta L_3 edge for Ta(N,O) films and the reference samples, Ta_2O_5, TaN, and Ta metal. The inset plots the Ta L_3-edge EXAFS oscillations.

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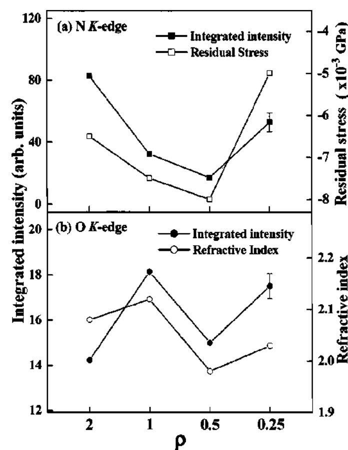

FIG. 4. (a) Integrated intensity in the π^* feature of the N K-edge spectra and residual stress as a function of ρ. (b) The integrated intensities of features A_2 and B_2 in the O K-edge near-edge spectra and refractive indices on ρ.

decreases as ρ is reduced from 2.0 to 0.5. This trend is understandable as one expects that the decrease of the N_2 flow rate decrease the N_2 content in the film, although the AES measurement indicated that the N/O content ratio decreases only slightly from 0.89 to 0.85. Since AES is sensitive only in the surface region, the AES N/O ratio may not accurately represent the N content in the film. The π^* integrated intensity rises up unexpectedly as ρ is further reduced from 0.5 down to 0.25. The intensity of the π^* feature in the N K-edge XANES spectrum generally depends on the environment and orientation of the molecule.[13,14] This unexpected rise may be caused by reorientation of the nitrogen molecules in boundary regions between Ta–O domains/fragments or surface region of the film, which is possible because the N_2 flow rate is much smaller. The AES N/O ratio decreases much faster from 0.85 to 0.74 with a small change of ρ of only 0.25, which indicates that AES is more sensitive for smaller ρ or N_2 flow rate. Thus, for smaller N_2 flow rate, N_2 molecules may reside closer to the surface, which may also be the reason for the rise of the π^* integrated intensity. The magnitude of the residual stress decreases with the increase of ρ from 0.5 to 2.0. This trend suggests that the N_2 containing boundary regions serve as flexible cushions to absorb the stress, so that the larger the N_2 content the smaller the magnitude of the residual stress. The great reduction in the magnitude of the stress for the smallest ρ of 0.25, which corresponds to the highest O_2 flow rate, suggest that the presence of N_2 molecules be the cause of dividing the film into small Ta–O domains/fragments and the reduction of the N_2 content in the film yields fewer and larger Ta–O domains/fragments and smaller residual stress.

Figure 4(b) plots integrated intensity of the O K-edge near-edge features (inset of Fig. 2) in the energy range between 528.4 and 542.6 eV. It also presents the refractive index data given in Table I. Figure 4(b) reveals that the integrated intensity of O K-edge near-edge feature varies similarly with the refractive index of the Ta(N,O) film. The O K-edge XANES intensity is proportional to the product of the density of unoccupied O $2p$–Ta $5d$ hybridized states and the transition probability between O $1s$ core and these unoccupied states. The transition probability in turn is proportional to the absolute square of the transfer matrices between these states. The refractive index, which is the square root of the product of dielectric constant and magnetic permeability, also depends on the transfer matrices between occupied and unoccupied O $2p$–Ta $5d$ hybridized states. The transfer matrices are integrals containing the wave functions of these O $2p$–Ta $5d$ hybridized states, which can be altered by not only the local Ta–O bonding arrangement but also N_2 containing boundary regions through long ranged electrostatic potential. Thus, the similar variation of the refractive index and the O K-edge XANES intensity suggests that the variation of the O K-edge intensity with respect to ρ cannot be directly interpreted as a variation in the density of unoccupied O $2p$–Ta $5d$ hybridized states. Jong *et al.* found very similar trend of the variation of the density and the refractive index.[11] Since Ta(N,O) films are composed of glassy Ta–O networks with N_2 molecules filled in boundary regions between Ta–O domains/fragments, the change in ρ is expected to alter the packaging of the Ta–O networks. Since Ta L_3-edge EXAFS data indicate that the NN Ta–O bond length remains the same in all the Ta(N,O) films, the variations in the density, refractive index and O K-edge intensity may be mainly due to changes in the local structures of the boundary regions between Ta–O domains/fragments, which include orientation and arrangement of N_2 molecules.

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