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Nitridation of organo-silicate glass: A self-limiting process for PVD $Ta_{1+x}N$/Ta barrier formation

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ABSTRACT

Interfacial reactions of sputter-deposited Ta with a low dielectric constant Si–O–C–H material (SiCOH), and with surface-nitrided SiCOH (N-SiCOH) were investigated using X-ray photoelectron spectroscopy (XPS). The studies were carried out in a system containing a processing chamber attached to an XPS analysis chamber so that sample transport between deposition and analysis environments occurred under ultrahigh vacuum (UHV) conditions. Ta sputter deposition on unmodified SiCOH yielded an interfacial phase ~3 nm thick composed of Ta oxide/carbide (Ta–O–C), which is known to interact only weakly with Cu. Bombardment of the vicinal SiCOH surface by 500 eV Ar^+ in the presence of NH_3 resulted in carbon depletion and the self-limiting nitridation of the surface, with N attachment primarily at Si sites. Subsequent Ta sputter deposition yielded reduced Ta oxide and carbide formation, and formation of a Ta-rich nitride layer of 10 Å average thickness. Subsequent deposition resulted in metallic Ta formation.

1. Introduction

Refractory metals and their nitrides have been identified as possible diffusion barriers for semiconductor applications due to their stability and excellent electronic conductivity [1,2]. Ta_2N/Ta binary barriers are widely used in the semiconductor industry to inhibit Cu diffusion through the dielectric and into the Si itself. The nitride layer inhibits diffusion while Ta–Cu interactions enhance interfacial adhesion. As barrier thicknesses continue to shrink to <5 nm, however, the reliable deposition of a binary barrier poses significant difficulties, including uniformity of film thickness and composition on topographically irregular SiCOH substrates. Several studies of reactive sputtering of tantalum in a N_2/Ar atmosphere [1,3,4] have shown that film composition is extremely sensitive to processing conditions. Lee et al. showed that a variation of the N_2/Ar flow ratio from 0.1 to 0.3 results in a sharp increase in the N/Ta ratio [4]. This narrow process window, especially for short deposition times mandated by nanoscale barrier thicknesses, may be problematic for industrial applications.

Although direct deposition of Ta is a potential alternative with simplified processing, previous studies [3,5,6] have shown that direct sputter deposition of tantalum on a SiCOH substrate forms an interfacial region ~3 nm thick with a composition of tantalum oxide and tantalum carbide, to which Cu does not strongly adhere. It should be emphasized that this interphase results from Ta–substrate *chemical* interaction, rather than physical diffusion of Ta into the dielectric [3,5]. This result places obvious chemical limitations on the minimum thickness of pure Ta barriers.

In this work, a self-limiting method is presented for the formation of an ultrathin Ta-rich nitride/Ta barrier by Ta sputter deposition on surface-nitrided SiCOH (N-SiCOH). The nitridation was carried out by low energy (500 eV) Ar^+ ion sputtering in the presence of a low partial pressure (10^{-6} Torr) of NH_3. The XPS data indicate that Ta deposition on N-SiCOH inhibits the Ta–O–C interphase formation and enhances the formation first of $Ta_{1+x}N$ and, at longer times, of metallic Ta.

2. Experimental

XPS experiments were performed in a combined UHV surface analysis/magnetron sputter deposition system composed of two independently turbomolecularly pumped chambers separated by a gate valve. Sample transport between the UHV analysis chamber (working pressure; $<6 \times 10^{-10}$ Torr) and deposition chamber

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(working pressure $<1 \times 10^{-8}$ Torr) was accomplished with a magnetically coupled rotary feedthrough. The analysis chamber was equipped with a 100 mm mean radius hemispherical analyzer (VSW) and dual anode polychromatic X-ray source (Physical Electronics) for XPS, and a differentially pumped Ar ion sputter gun (Specs) for sample cleaning. A thermal cracker (Oxford Applied Research) was used for exposure to partially dissociated NH_3, yielding a mixed flux of molecular and dissociated ammonia and atomic H; NH_x+H (x = 1–3). Pressure in the analysis chamber was monitored by a nude ion gauge out of line of sight to the sample. Sample temperature was controlled by a combination of liquid nitrogen cooling and resistive heating between 150 and 1200 K, with sample temperature monitored by a type K thermocouple mounted just below the base of the sample transfer platform. Separate calibration experiments, in which a thermocouple was also mounted to the surface of the sample, were used to characterize the temperature gradient (approximately 100 K over a broad temperature range) between sample surface and sample mount base. Temperatures reported here are those for the sample surface. The deposition chamber was equipped with water-cooled DC-Magnetron sputter deposition source (Minimack). Ar was admitted to the chamber through a manual leak valve with the gas pressure monitored by nude ion or baratron gauges. Sputter deposition rates were measured by subsequent XPS analysis, as detailed previously [3], and varied by adjustments of source/sample distance or gas pressure. Sample temperature was not controlled during deposition. XPS spectra were acquired with polychromatic Mg Kα radiation with the source operating at 15 kV and 300 W and the hemispherical analyzer operated in constant pass energy mode (22 eV). Since sample charging was frequently observed during XPS analysis, binding energies were calibrated by setting the C(1s) level of the substrate at 285.0 eV [2]. XPS data were analyzed using commercially available software (ESCA-TOOLS) and Shirley background subtraction. In simulating spectra for comparison to experiment, Gaussian–Lorentzian peaks were used. During peak fitting, binding energies and FWHM values were fixed, and only intensities were permitted to vary. The FWHM value used in this study for Ta metal (1.33 eV), was determined by measurements on polycrystalline metallic Ta in this system under identical instrumental conditions. A different FWHM value was used for Ta oxide and nitride features (1.55 eV) due to a widening of the XPS feature that could not be fit properly using the FWHM for metallic Ta. Ta sputter deposition was carried out using Ar plasma with a pressure of 15 mTorr. Ta was deposited from a 99.999% purity Ta target at a deposition rate of 1.3–0.2 Å min^{-1} with the deposition rate controlled by changing the plasma power level. All the depositions were performed at room temperature. The deposition rate was determined for Ta deposition by measuring the attenuation of the Si(2p) substrate signal according to [7]:

$$I = I_0 \exp^{(-d/\lambda)} \tag{1}$$

where d is the average thickness of the overlayer, and I_0 and I are the absolute Si(2p) core-level signal intensities before and after Ta deposition, respectively. λ is the calculated electron inelastic mean-free path (IMFP) [8] for (in this case) a Si(2p) electron through Ta, or Ta_2O_5, with values of 14.22 Å, and 20.10 Å, respectively. The thickness of the attenuating overlayer was calculated by plotting the below equations with increasing overlayer thicknesses (d):

$$I_B = I_B^{\infty}\, e^{(-d/\lambda \cos\theta)} \tag{2}$$

vs.

$$I_A = I_A^{\infty}[1 - e^{(-d/\lambda \cos\theta)}] \tag{3}$$

where I_A and I_B are the intensities of the attenuating overlayer and the substrate respectively. Similarly, I_A^{∞} and I_B^{∞} are the atomic sensitivity factors for the attenuating overlayer and the substrate, respectively [7]. Absolute, rather than relative Si(2p) intensities were measured. The error in measuring absolute intensities in this apparatus has been determined to be <10%, by repeated measurements on the same sample [3]. This approach of course assumes negligible incorporation of Si into any growing Ta overlayer, as determined by previous studies [2,3,5] and verified by our results (see below). The nonporous SiCOH wafers used in the XPS portion of this study were 4200 Å thick, deposited on Si substrates, and displayed a dielectric constant of 2.9. Each wafer was cut into multiple pieces ~1 cm^2 and mounted on a Mo sample holder for surface science studies, and inserted into vacuum without further treatment.

3. Results

3.1. Ta deposition on vicinal SiCOH

Tantalum was sputter deposited onto a clean, unmodified SiCOH substrate with a deposition rate of 1.3 Å min^{-1}. Fig. 1 shows the Si(2p), O(1s), C(1s) and Ta(4f) XPS spectra before (Fig. 1a–d, top trace) and after (Fig. 1a–d, bottom trace) 3 min of Ta deposition. The Si(2p) spectrum prior to deposition (Fig. 1a, top trace) consists of two features with binding energies of 103.5 and 102.5 eV. These binding energies are consistent with Si–O [1–3,5] and Si–C [3,5] bonding environments, respectively. The O(1s) spectrum (Fig. 1b, top trace) also consists of two features at 533 and 532.2 eV, corresponding to O–Si and O–C [2,3], respectively. Similarly the C(1s) spectrum consists of two feature at 285 and 284.2 eV attributed to C–C and C–Si [2,3] interactions.

Upon Ta deposition, the entire Si(2p) feature (Fig. 1a, bottom trace) is attenuated with no change in peak binding energy, but significant change in peak shape. A marked reduction in the feature corresponding to Si–C is observed. For both the O(1s) and C(1s) spectra, a slight attenuation is observed. A new feature is also observed in the O(1s) spectrum (Fig. 1b, bottom trace) with a binding energy of 530.7 eV. This feature corresponds to the formation of Ta oxide [3,5]. Similarly, a new feature is seen in the C(1s) spectrum (Fig. 1c, bottom trace) after deposition, with a binding energy of 282.8 eV, which corresponds to TaC [3–5]. These feature assignments are corroborated by the appearance of features in the Ta(4f) spectrum (Fig. 1d, bottom) corresponding to TaO_x (24.8 eV) and TaC (23.3 eV), respectively. Metallic tantalum was observed after ~9 min deposition (not shown), as evidenced by a feature at 22.1 eV in good agreement with previous results [3,5]. Using the attenuation of the Si(2p) feature, the thickness of the Ta–O–C overlayer formed prior to the observation of metallic Ta formation was calculated to be ~3 nm, in good agreement with previous results [3,5].

3.2. Nitridation of SiCOH and Ta deposition on N-SiCOH

Fig. 2 displays the evolution of XPS-derived Si/O and C/Si atomic ratios as a function of Ar$^+$ bombardment (1×10^{-5} Torr Ar, 500 eV) sputtering in the absence, and then in the presence of an NH_3 background pressure (1×10^{-6} Torr). Initial Ar$^+$ sputtering in the absence of NH_3 results in the removal of carbon from the surface region, as indicated by the monotonic decrease in the C/Si atomic ratio (derived from XPS intensities) without change in the Si/O atomic ratio. After 50 min Ar$^+$ ion bombardment under these conditions, no further change in Si/O or C/Si atomic ratio is observed. After the addition of NH_3 to the chamber during the sputtering process, additional loss of C is observed, although a new steady-state situation is achieved after additional bombardment (Fig. 2).