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Reversible Tuning of the Surface Chemical Reactivity of Titanium Nitride and Nitride−Carbide Diffusion Barrier Thin Films

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The chemical properties of titanium nitride−carbide (TiNC) and titanium nitride (TiN) films deposited on silicon are investigated comparatively, showing that the surface reactivity of nitride-based films can be modified precisely and reversibly by controlling the surface elemental composition. These materials are used as diffusion barrier films, and therefore understanding their surface chemistry is key for controlling further deposition steps during interconnect metallization. Chemical vapor deposition (CVD) using $Ti[N(CH_3)_2]_4$ leads to the formation of TiNC, and nitridation of this film through postannealing under NH_3 decreases significantly the carbon content on the surface, leaving essentially a TiN surface, as characterized through the use of spectroscopic, depth-profiling, and microscopic techniques. As determined by the temperature-programmed desorption (TPD) studies of ethylene (carbidization reagent) and dimethylamine (decomposition product of the deposition precursor), the TiN surface is more reactive toward these compounds than the original TiNC film. The role of carbon as a surface reactivity modifier is explained by its ability to decrease the acidity of Ti surface atoms. Moreover, the test reaction of ethylene on the TiN surface is accompanied by a decomposition process that progressively incorporates carbon onto the surface, reducing the surface reactivity to the point where it resembles that of the starting TiNC film. The ability to control the reactivity of a deposited film offers unique opportunities in designing chemical modification schemes for a successful deposition onto these barrier films.

I. Introduction

The microelectronics industry relies on metal nitrides as barrier films against the diffusion of metals into semiconductor components in integrated circuits.[1−3] For instance, TiN possesses excellent properties against the diffusion of aluminum or tungsten,[1,4] and copper diffusion can be avoided by using TaN and WN.[5−9] In addition, metal nitrides are usually employed as adhesion promoters (e.g., TiN as a “seed layer” for W deposition).[10,11]

Since carbon increases the resistivity of barrier films,[3,12] several strategies were developed to reduce the +carbon content in nitride films, including the use of easily controllable film deposition techniques (such as atomic layer deposition, ALD)[2,5,7−9,13−16] and the implementation of postdeposition (e.g., plasma[4,17−20] and thermal[21−23]) treatments. However, interest in nitride−carbide films has been boosted recently because the crystallinity of pure nitrides is disrupted by the presence

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of carbon, avoiding potential diffusion through grain boundaries.[15,24,25] Tungsten nitride−carbide (WNC) is currently receiving considerable attention as a copper diffusion barrier,[24−27] and nitride−carbides of titanium (TiNC) and tantalum (TaNC) have been investigated for this purpose as well.[20,28−34] Oxygen incorporation, which also increases the resistivity of these films and occurs readily upon exposure to ambient atmospheric conditions following vacuum deposition, is a more persistent problem that has also received substantial attention.[4,14,17,20,28,35−37]

From a chemical point of view, a diffusion barrier film must feature an appropriate surface reactivity toward the precursors used to deposit a metal in the next stages of interconnect metallization.[11] At the same time, the barrier film is expected to have a limited reactivity toward contaminants that can threaten the performance of the device and to be chemically resistant during other stages of processing, for example, during chemical-mechanical polishing.[10] As a result of the different levels of reactivity needed for these films at different processing stages, it is desirable to develop strategies to ensure a versatile chemical behavior of surfaces of nitride and nitride−carbide thin films. In the present investigation such versatility is achieved, as confirmed by following the reaction of these films with simple model molecules, which in turn provide a platform for future studies involving more complex compounds of technological relevance. Although the surface chemistry of nitrides and carbides has been studied extensively, previous studies have largely focused on substrates with well-defined orientations,[35,38−43] which is not the case for as-deposited diffusion barrier films. Insightful investigations on the surface reactivity of deposited TiN films have been reported,[21,44−46] but in most cases there is a significant presence of carbon, and as will be shown here, this element affects substantially the surface reactivity of a film.

II. Experimental Methods

A. Film Deposition. Deposition of films and thermal desorption experiments were performed in an ultrahigh vacuum chamber (base pressure below 10^{-9} torr) equipped with a shielded differentially pumped mass spectrometer (Hiden Analytical) employed to test the purity of the precursors and to perform temperature-programmed desorption (TPD) experiments. In addition, this chamber is outfitted with an Auger electron spectrometer (Staib Instruments) to verify the cleanliness of the surface and the composition of the films. The precursor tetrakis(dimethylamido)titanium ($Ti[N(CH_3)_2]_4$ or TDMAT; Epichem, 99.99%) was purified using several freeze−pump−thaw cycles, and its purity was confirmed *in situ* by mass spectrometry. TiNC test films were deposited by exposing a Si(100) substrate to 5000 L of TDMAT ($1\ L = 10^{-6}$ torr·s) at 620 K; further annealing to 800 K allowed the elimination of trapped organic fragments.[21,32] Annealing of the TiNC film to 900 K under NH_3 for 10 min (approximate dose of 6000 L) has been shown to eliminate most carbon from the surface,[22,23] leaving essentially a TiN film.

Ex situ characterization techniques included X-ray photoelectron spectroscopy, XPS (PHI-5600, using an Al Kα monochromatic X-ray source with $h\nu = 1486.6$ eV and a hemispherical analyzer tilted 45° from the substrate plane); transmission electron microscopy, TEM (JEOL JEM-2010F, operating at 200 kV and with images collected using a Gatan multiscan CCD camera); atomic force microscopy, AFM (Veeco multimode SPM with a NanoScope IIIA controller and BS-Tap 300Al tips, tapping mode); and depth profiling time-of-flight secondary ion mass spectrometry, ToF-SIMS (TOFSIMS IV ION-TOF, using a 1-keV Cs^+ sputter gun and a 25-keV monoisotopic $^{69}Ga^+$ primary ion beam for sample analysis). Additional details of the characterization procedures are provided elsewhere.[31,34]

B. Temperature-Programmed Desorption (TPD) Experimental Details. After the films were deposited, dimethylamine, the main decomposition product of TDMAT, was present as background gas and was able to adsorb on the films.[45] Adsorbed dimethylamine was eliminated by flash-annealing the substrates to 800 K after the base pressure had returned to the 10^{-9} torr range. The reactivity of TiNC and TiN surfaces was tested using deuterated ethylene (C_2D_4, Sigma-Aldrich, 99% isotopic purity). The choice of C_2D_4 over C_2H_4 was made because the latter has a mass fragmentation pattern that overlaps with that of carbon monoxide, an adventitious background gas that interferes with the TPD analysis. By exposing the film to 1000 L of C_2D_4 at 300 K, a saturated chemisorbed layer was obtained. The sample surface was positioned approximately 2 mm from the inlet aperture of the shielded differentially pumped mass spectrometer for TPD studies. The heating rate in the TPD experiments was 2 K/s in all cases. Peak desorption temperatures

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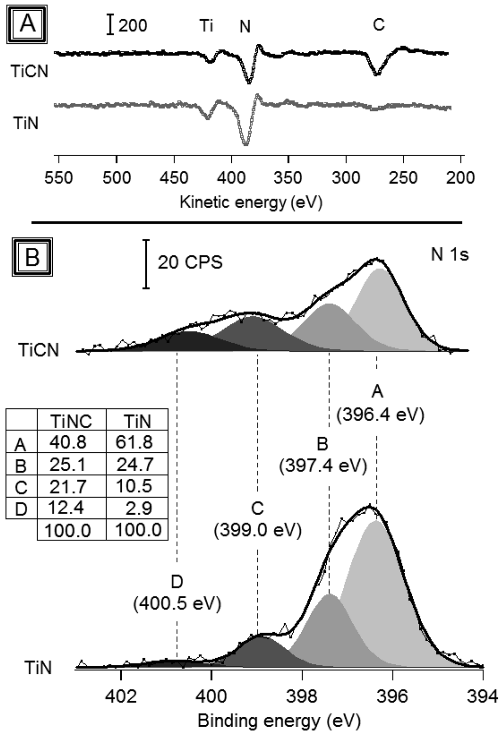

	TiNC	TiN
A	40.8	61.8
B	25.1	24.7
C	21.7	10.5
D	12.4	2.9
	100.0	100.0

Figure 1. Characterization of TiNC and TiN films by in situ AES (part A) and ex situ XPS (part B). The in situ AES experiments show that the carbon content in TiNC is decreased drastically through ammonia postannealing. As described in the text, the N 1s XPS spectra for both films were fitted using four components: A and B, associated with nitride, and C and D, associated with an organic matrix. The inset chart shows that after ammonia postannealing the presence of nitride increases and the organic nitrogen fades. Additional XPS data can be found as Supporting Information.

were employed to estimate desorption activation energies using the Redhead method,[47] assuming a first-order reaction and a commonly used pre-exponential factor of 10^{14} s^{-1}.

C. Density Functional Calculations. Adsorption energies for ethylene and dimethylamine were predicted using surface models based on the $Ti_4N_2C_2$ cluster, which has been previously used as a simplified representation of a TiNC surface.[32,33] Single-point energies are calculated at the B3LYP/6-311+G(d,p) level of theory, based on geometries obtained at the B3LYP/LANL2DZ level. All calculations were performed using the Gaussian 03 suite of programs.[48]

III. Results

A. Characterization of Films and Evidence of the Transformation from TiNC to TiN. Films deposited using an exposure of 5000 L of TDMAT were approximately 10 nm thick (vide infra) and transparent upon visual inspection. However, thicker TiNC films (obtained with TDMAT exposures above 20 000 L) were blue-colored, turning to golden after postannealing in NH_3. This change has been attributed to the phase change,[49] constituting the first evidence of the surface transformation from nitride–carbide to nitride.

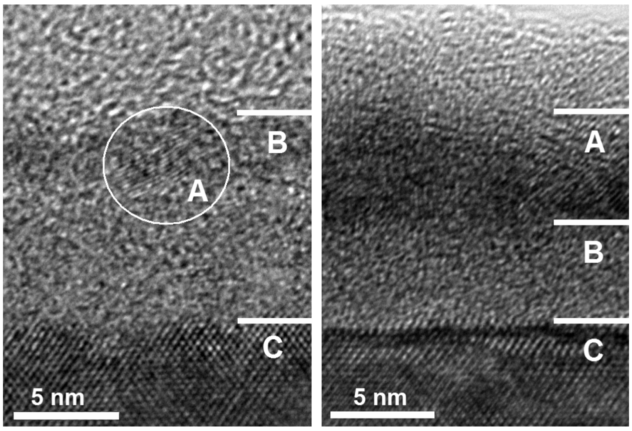

Figure 2. Cross-sectional TEM micrographs of a TiNC film before (left) and after (right) NH_3 postannealing. The TiNC film (left) is composed of crystalline nanostructures (A) embedded into an amorphous matrix (B) deposited onto a single crystalline silicon substrate (C). Upon NH_3 postannealing to produce TiN (right), the top layers of the film were mostly polycrystalline (A) and the inner portion of the film (B) above the single crystal silicon (C) remained amorphous.

Figure 1A shows the Auger spectra of a TiNC film before and after the postannealing treatment, verifying in situ the change in surface composition and the formation of TiN, as evidenced by the near-disappearance of the C *KLL* Auger feature at 272 eV. It is worth mentioning that oxygen was not observed in any of the films, indicating that high-purity TiNC and TiN films were deposited. The ex situ N 1s X-ray photoelectron spectra of both films, Figure 1B, was fitted using four components, A through D, located respectively at 396.4, 397.4, 399.0, and 400.5 eV. Previous in situ studies have related the components around 396.0 (component A) and 399.0 eV (component C) to nitrogen bound to Ti[30,50-52] and to nitrogen embedded in an organic matrix,[51,52] respectively. It is possible that the components observed at 397.4 (component B) and 400.5 eV (component D), neither of which were reported in the in situ experiments mentioned, were due to the oxidation of nitride and organic components, respectively, upon exposure of the films to ambient conditions. A quantitative analysis of the total nitrogen content of the film's surface based on these assignments was performed (see Supporting Information for more details) and is included in Figure 1B. Our analysis indicates that upon NH_3 postannealing, the nitrogen content (normalized with respect to the Ti signal) increased by approximately 40%, supporting film nitridation, with the nitrogen present as nitride (component A) increasing in relative intensity by 51.5% and with the "organic" nitrogen (component C) decreasing in relative intensity by 51.4%. This analysis supports the elimination of organic carbon present in the nitride–carbide film. Although direct proof of the elimination of carbon could be potentially obtained from the analysis of the C 1s XPS spectrum, exposure of the films to ambient conditions resulted in an uptake of carbon that made such analysis

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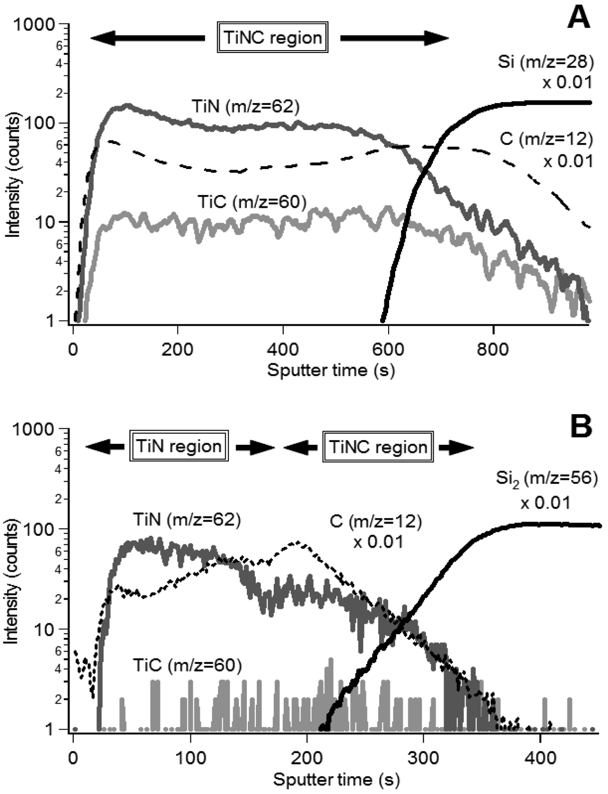

Figure 3. ToF-SIMS positive-ion depth profiles of a TiNC film (A) and a TiNC film after NH_3 postannealing (B). The steady presence of TiC and TiN signals in (A) before the interface (~600 s) indicates a uniform composition throughout the deposited film prior to NH_3 postannealing. After postannealing (B), the TiC signal is almost negligible, indicating that C bound to Ti has been reduced drastically, producing a surface enriched in TiN. An increase of the $m/z = 12$ signal (carbon) close to the interface with the silicon substrate (~200 s) coincided with the decrease of the $m/z = 62$ signal (TiN), suggesting that nitridation does not occur through the entire film, in agreement with TEM. Additional ToF-SIMS data can be found as Supporting Information.

ambiguous. The reader is referred to the Supporting Information for a brief discussion regarding other XPS spectral regions (C 1s, O 1s, and Ti 3p).

Cross-sectional TEM micrographs (Figure 2) show that the TiNC can be described as an amorphous film, where some nanocrystallites are embedded, in agreement with previous studies.[31,34] After nitridation, the top portion of the film increased in crystallinity, while the bottom of the film remained predominantly amorphous. This indicates that nitrogen from ammonia penetrated into the film and produced a structural change, leading to the formation of a relatively sharp nitride/nitride–carbide interface. The micrographs show similar silicon/film interfaces in both cases, indicating that the postannealing treatment does not threaten the integrity of such an interface. The surfaces of both films were found to have a similar roughnesses by AFM (rms roughness of 0.60 nm for TiNC and 0.48 nm for TiN, within a sample area of 3× 3 μm^2).

Depth profiling ToF-SIMS spectra (Figure 3) show that the $m/z = 60$ trace (associated with TiC^+ fragments), present in the original film, was almost absent in the TiN film obtained after postannealing in NH_3. More importantly, the depth profile of the TiN film shows two regions: a TiN-rich top zone and a carbon-rich region close to the silicon substrate interface, as evidenced by the increase of the $m/z = 12$ signal, corresponding to elemental carbon, and by the decrease of the $m/z = 62$ signal, corresponding to TiN^+. Since the analysis has been performed *ex situ* and knowing that the two different films have different oxidation rates (which leads to the presence of TiO^+ species in the spectra), a more detailed comparison of the depth profiles of the films is impractical based on these results. Other depth profiles are included as Supporting Information and further support the success of nitridation.

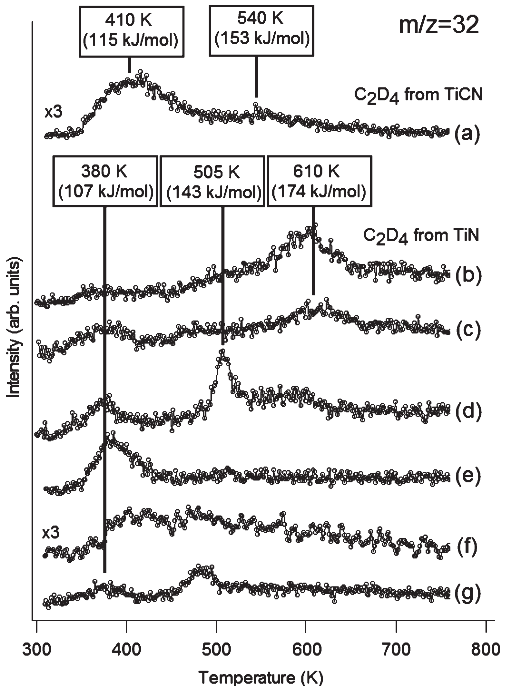

Figure 4. Temperature-programmed desorption of C_2D_4 from TiNC and TiN. In all cases, the molecular mass $m/z = 32$ ($C_2D_4^+$) was followed after exposing the surface to 1000 L of C_2D_4 at 300 K, using a constant heating rate of 2 K/s. (a) Desorption from a freshly prepared TiNC surface; (b) desorption from a freshly prepared TiN surface; (c–f) representative desorption spectra showing changes in the desorption channels as a result of two, five, six, and seven consecutive experiments performed on the same TiN surface, respectively; and (g) desorption from a TiN surface after seven consecutive adsorption/desorption cycles and a light sputtering to remove incorporated carbon, showing similarity to spectrum (d).

By using the combined information of several characterization techniques we have confirmed that the NH_3 postannealing treatment modified the composition of a TiNC film through the incorporation of nitrogen into the top layers of the film, decreasing the content of carbon and increasing that of nitrogen. The top of the film became more crystalline due to the nitridation of the film and, accordingly, XPS showed an increase of the nitride component in the N 1s spectrum. Nitridation did not affect substantially the smoothness of the films nor the structural quality of the interface with the silicon substrate.

B. Evidence of Changes in Surface Reactivity of TiNC and TiN Films. As shown in Figure 4, spectrum (a), ethylene desorption from TiNC was observed with maxima

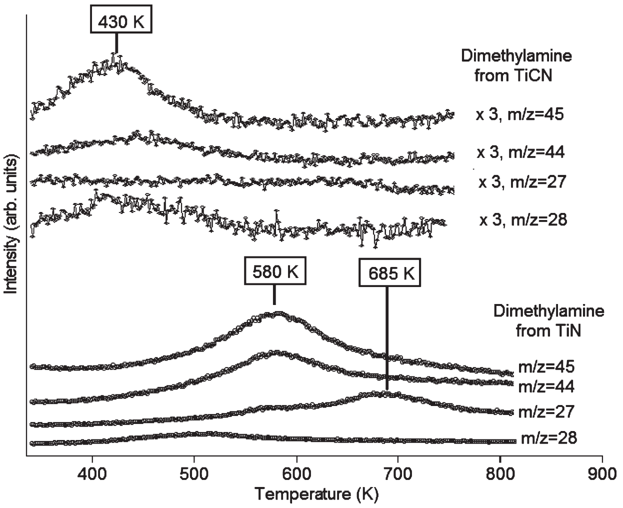

Figure 5. Desorption of dimethylamine from TiNC (top set of data) and from TiN (bottom set of data). In both cases, desorption channels corresponding to the molecular mass ($m/z = 45$) and the most representative mass fragments ($m/z = 44$, 28, and 27) are shown.

at 410 K and at 540 K. Activation energies for desorption calculated using the Redhead method are 115 and 153 kJ/mol, respectively. These two desorption channels have been previously attributed to the attachment of alkene molecules to Ti−C diatomic sites and to Ti sites, with the former yielding a lower desorption energy than the latter.[32] Subsequent ethylene desorption experiments that were repeated up to seven times from the same TiNC surface resulted in essentially identical desorption traces suggesting that ethylene desorption is the major process on this surface and that ethylene decomposition does not occur on TiNC to a significant extent at these conditions.

Desorption of C_2D_4 from a freshly prepared TiN surface, spectrum (b) in Figure 4, occurred only through one desorption channel, at 610 K (Redhead activation energy for desorption was 174 kJ/mol). The absence of a significant desorption channel at 410 K observed on a freshly prepared TiNC surface demonstrated that such a desorption channel must have originated from the presence of carbon on the surface, highlighting the important role that carbon plays in altering the reactivity of a nitride surface. TiNC films adsorbed approximately 66% less ethylene than TiN films of the same area, indicating that the adsorption process is hindered for the nitride−carbide film. Since both films possessed a similar roughness (*vide supra*), the difference in the amount of material adsorbed/desorbed cannot be attributed to a difference in roughness-induced sample surface area. It is likely that the TiNC surface was composed not only of Ti-containing reactive sites but also of nonreactive surface sites, consisting mostly of carbon and nitrogen, on which very little adsorption could take place. In this regard, it has been previously stated that these elements can block the metal sites present on a surface.[42] As this "organic" phase was eliminated during heat-induced nitridation in NH_3, the surface consisted of an increasing number of Ti-containing reactive sites, and consequently the nitridized surface may be able to reactively adsorb a larger number of molecules.

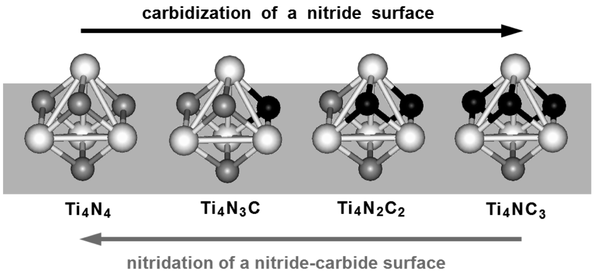

Figure 6. Cluster models simulating the surface sites of deposited films of TiN and TiNC, where a surface Ti atom (above the gray box) has different neighbors. White: titanium, gray: nitrogen, black: carbon. Predicted adsorption energies shown in Table 1 were obtained by attaching the adsorbates to the surface Ti atom above the gray box.

The sensitivity of the TiN surface to carbon incorporation was also analyzed by performing successive adsorption−desorption experiments on the same surface. Figure 4c−f shows that as consecutive adsorption−desorption experiments were performed, a change in the desorption channels was observed in the TPD spectra. A desorption feature started to develop at around 380 K, while the original desorption feature observed at 610 K shifted to lower desorption temperatures and finally disappeared after approximately the fifth adsorption−desorption cycle. This indicated that the TiN adsorption sites became less reactive or less abundant due to the decomposition of ethylene and the incorporation of carbon into the surface. This *surface* transformation from nitride to nitride−carbide occurred gradually and seemed to be completed after seven consecutive adsorption−desorption experiments. The desorption spectrum from the TiN surface after seven adsorption−desorption cycles (f) resembled the one from the TiNC surface (a) in both shape and intensity. The decrease in desorption intensity from (b) to (f) suggests that carbon atoms incorporated into the film block reactive Ti surface atoms. Thus, partial decomposition of ethylene resulted in the carbidization of the TiN surface, a process that we suggest can be employed to tune the surface reactivity of the film.

After a brief Ar^+ sputtering of the carbidized TiN surface (under 10^{-6} torr Ar, at 1 keV for 5 min), the thermal desorption spectrum of ethylene (Figure 4g) exhibited a pattern similar to that observed after five adsorption−desorption cycles (Figure 4d), showing that after eliminating the first layers of carbidized TiN, the underlying sites were still nitride-like and that carbidization is largely a surface process that does not affect the bulk of the TiN film. It should be noted, not surprisingly, that this sputtering procedure affected the roughness of the film (the rms roughness of the sputtered surface was $\sim$2.0 nm for a sample area of 3×3 μm^2).

Incorporation of carbon into a TiN film by decomposition of C_2D_4 implies that hydrogen desorption (as D_2) ought to be observed. Although there was some evidence of D_2 desorption above 800 K, the intensity of the corresponding TPD signal was very low. However,

Table I. Adsorption Energies (kJ/mol) for Ethylene and Dimethylamine Predicted by DFT Calculations Using the Cluster Models Shown in Figure 6[a]

	density functional theory calculations				TPD experiments	
	Ti_4N_4	Ti_4N_3C	$Ti_4N_2C_2$	Ti_4NC_3	E_{des} from TiN	E_{des} from TiNC
ethylene	−155.4	−105.9	−106.8	−81.9	−174	−115
dimethylamine	−151.6	−131.0	−121.2	−109.4	−165	−121

[a] In all cases, molecular adsorption was confined to take place on a Ti atom. Values are reported with respect to the added energy of the cluster model and a free adsorbate and were obtained from single-point calculations (B3LYP/6-311+G(d,p)) using optimized geometries (B3LYP/LANL2DZ). The absolute value of the reported quantity (in kJ/mol) can be regarded as the heat of adsorption, ΔH_{ads}, which, in the absence of an adsorption activation barrier, can be compared to the desorption activation energy E_{des} calculated through the Redhead analysis of the TPD data (right columns).

additional insight into the possibility of decomposition on TiN can be obtained by comparing the TPD profiles during the flash-annealing of the surface to eliminate the adsorbed dimethylamine (as indicated in Section II). Figure 5 shows these profiles, where the difference in desorption temperatures and intensities again confirmed the higher reactivity of the TiN surface relative to the TiNC surface. Desorption energies of 121.4 and 165.2 kJ/mol calculated based on the Redhead method were observed for TiNC and TiN, respectively. More importantly, it can be noted that while for TiNC the desorption of dimethylamine (m/z = 45; $C_2H_7N^+$) was observed together with other fragments (m/z = 44, 28, 27), an additional desorption channel was observed on TiN (m/z = 27; HCN^+) at 685 K. The absence of a molecular desorption channel at this temperature suggested that HCN, a typical product from surface decomposition of dimethylamine,[53] evolved from the surface. Ammonia has been observed to desorb at 640 K from an as-deposited TiN surface, with hydrogen evolving at 740 K.[54] Evolution of H_2 from NH_3 decomposition has been observed previously from a deposited TiN film,[21] as well as from molybdenum nitride.[55] Thus, it is apparent that, different from the TiNC surface, the TiN surface exhibits a greater reactivity toward some adsorbates, as will be discussed next.

IV. Discussion

A. Surface Composition−Reactivity Relationship. Although the specific nature of surface sites and the exact mechanism of adsorption are difficult to elucidate, it is likely that reactive surface sites involve a Ti surface atom, either as a corner site or as a Ti−C surface site.[32,33,39,54] Ethylene and dimethylamine react as Lewis bases, and their adsorption mechanisms involve the attack of the π-bond electrons and the N lone-pair electrons, respectively, onto a Ti atom on the surface.[46,54,56,57] On the basis of this analysis, reactive adsorption should be more favored when Ti atoms are more acidic or electron-deficient. The electron deficiency of Ti is enhanced by the presence of relatively more-electronegative N atoms surrounding the Ti surface sites. Conversely, as relatively less-electronegative C atoms are introduced into the surface, Ti atoms become less electron-deficient, or less acidic.[57,58] However, the fact that dimethylamine (which has a greater electron-donating ability than ethylene) desorbs at lower temperature than ethylene may indicate that electron back-donation from the Ti atom to the C_2D_4 molecule takes place and contributes to enhanced adsorbate−substrate bonding, as described by the Dewar−Chatt−Duncanson model.[59,60] It has been previously stated that this happens when the Ti sites feature a metallic character, with Ti bound to N having a greater metallic character than Ti bound to C.[29,39] The lesser metallic character of Ti−C sites would also explain the observed weaker adsorption on TiNC sites. A detailed analysis of the reactivity of amines and π-donors on crystalline TiN and TiC surfaces has been performed by Didziulis et al.[39]

Regardless of the explanation for the adsorbate−substrate bonding, it is clear that carbon decreases the surface reactivity toward Lewis bases of nitride films. The effect of the carbon content on the surface reactivity was explored through density functional theory calculations. Different surface sites were represented with clusters following the general formula $Ti_4N_XC_{4-X}$, as shown in Figure 6. Predicted adsorption energies for ethylene and dimethylamine on a Ti atom surrounded by different numbers of C and N atoms are summarized in Table 1. They show a very good general agreement with the energies obtained based on the Redhead analysis of the TPD data. Especially noteworthy for our purposes is to highlight the decreasing trend of predicted adsorption energies as a “nitride” site is transformed into a “nitride−carbide” site, in agreement with our experimental observations.

B. Implications for Film Processing. Once deposited, a diffusion barrier film can be subjected to several different processes, such as metal deposition, exposure to ambient, or etching. Each of these processes demands a specific set of chemical properties that may not be appropriate for another process (e.g., low reactivity if exposed to ambient atmospheric conditions, higher reactivity for further deposition steps or for etching). This work has shown that the surface reactivity of diffusion barrier films can be tuned through the control of the carbon content in the top layers. With metal nitride−carbides gaining more

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attention,[15,24,25] it is important to realize that, although those materials often feature a lower reactivity (toward Lewis bases) than that of carbon-free metal nitride films, nitridation of the top layers of nitride–carbide films would constitute a simple but effective way to enhance their surface reactivity. On the other hand, the reactivity of a carbon-free metal nitride film can be lowered through the partial carbidization of its surface sites. We have shown here that this process can take place progressively and controllably through the decomposition of ethylene. This constitutes a gentle procedure that does not affect significantly the composition and interfacial properties of the bulk of these films. NH_3 postannealing modifies the bulk composition of the film but does not seem to affect the film–substrate interface. Unlike the two previous processes, sputtering affects the roughness of the film and may not be an adequate technique for surface composition modification. Nevertheless, the use of more gentle, precise techniques may allow one to achieve an adequate tuning of the surface reactivity of nitride-based films without compromising the physical properties of the film. An interesting speculation based on the present investigation is the formation of alternating layers of amorphous/crystalline (or insulating/conducting) layer-zones within the film. This would help not only to retain the ability to control the surface reactivity but also to control the physical and mechanical properties of a diffusion barrier film. Further investigations will be necessary to corroborate this suggestion.

V. Summary

It has been shown that the surface chemical reactivity of the diffusion barrier films TiNC and TiN could be tuned through the variation of the carbon content in the near-surface layers of the film. Ammonia postannealing of TiNC films transformed the top layers into TiN, increasing the surface reactivity of the film toward ethylene and dimethylamine. Repetitive cycles of ethylene decomposition on TiN films progressively introduced carbon into the near-surface region of the films, gradually reversing the surface reactivity of the TiN layers up to the point where it resembled that of the original TiNC film. Finally, brief low-energy argon-ion sputtering was found to remove almost all of the carbon incorporated into the carbon-enriched TiN film, returning it to the original TiN reactivity levels. We suggest that the role of carbon in TiN_xC_y films can be understood by considering that this element decreases the Lewis acidity and/or the metallic character of the surface Ti atoms. The reversible control of surface chemical properties shown here creates a possibility for the design of chemical modification schemes based on gas-phase deposition and decomposition on top of these films.

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Supporting Information Available: XPS spectra for Ti, C, and N, AFM images, additional ToF-SIMS data, and Cartesian coordinates of predicted adsorption structures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.