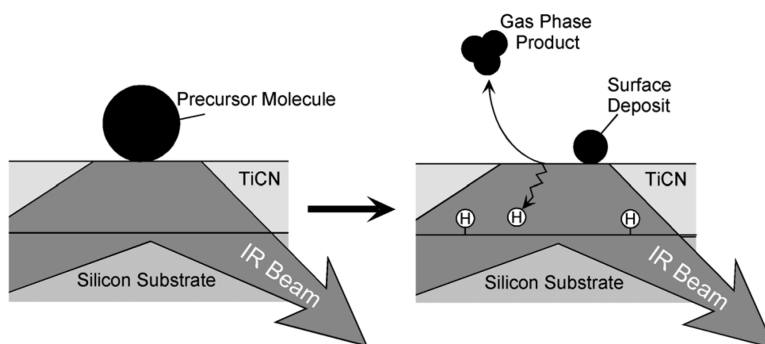


Spectroscopic Evidence for Hydrogen Diffusion through a Several-Nanometers-Thick Titanium Carbonitride Layer on Silicon

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J. Am. Chem. Soc., **2003**, 125 (24), 7196-7197 • DOI: 10.1021/ja035026f • Publication Date (Web): 23 May 2003

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Spectroscopic Evidence for Hydrogen Diffusion through a Several-Nanometers-Thick Titanium Carbonitride Layer on Silicon

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Barrier films are often used in electronics to prevent interdiffusion of metals and silicon. Titanium nitrides and carbonitrides are known to be stable as a diffusion barrier between Cu and Si at temperatures as high as 650 °C.^{1–6} They can be produced using chemical vapor deposition schemes, which may be very important for future low-temperature processing. In fact, titanium carbonitride was reported to have a set of very attractive physical properties and better conformal filling than titanium nitride.^{7–9} However, one of the factors that may affect the thermal stability of these films is the presence of hydrogen. Since the majority of analytical methods used in barrier layer analysis are focusing on topography and depth-profiling, the presence of hydrogen at the TiCN/Si interface is not normally observed. As will be shown below, the thermal chemistry of hydrogen on silicon surfaces suggests that hydrogen molecules may be responsible for the breakdown of the diffusion barrier. The major question is how to detect the presence of hydrogen at the interface and follow its evolution.

Here we report what is, to our knowledge, the first spectroscopic observation of the room-temperature hydrogen diffusion through a ~10-nm-thick titanium carbonitride film deposited onto a Si(100)-2×1 surface. Multiple internal reflection Fourier transform infrared spectroscopy (MIR FT-IR) is used as a diagnostic tool to follow hydrogen transformation on a surface of a Si(100)-2×1 single crystal precovered with a ~10-nm-thick layer of titanium carbonitride. The course of the experiment is outlined in Scheme 1. The TiCN film was deposited in our experiments at 593 K (320 °C) using tetrakis(dimethylamino)titanium ((N(CH₃)₂)₄Ti; TDMAT) as a precursor. High carbon content (from 25 to 35 at. % in these experiments, as confirmed by Auger electron spectroscopy, AES) is consistent with the previous studies.^{10,11} The AES studies also confirmed the absence of silicon in the topmost layers, which suggests that the film produced is continuous. The thickness of the carbonitride layer was estimated to be ~10 nm on the basis of the ex situ time-of-flight secondary ion mass spectrometry and atomic force microscopy (AFM) studies performed at the Surface Analysis Facility at the University of Delaware. The root-mean-square roughness of this film was estimated to be ~3-nm on the basis of AFM studies. Previous studies of TiCN films deposited from tetrakis(dialkylamino)titanium precursors at conditions similar to ours suggest that these films have amorphous structure, which is one of the main reasons why this approach leads to better conformal filling and a smoother surface than in the case of titanium nitride or titanium carbonitride with a low carbon content.¹¹ The detailed structure of the films produced by such an approach in our studies is the subject of a separate publication.¹²

MIR FT-IR studies of such a system provide detailed spectroscopic information not only about the chemistry of the titanium carbonitride surface but also about the TiCN/Si interface in one spectroscopic measurement.

Scheme 1. Application of Internal Reflection FT-IR To Study a Multilayered System of TiCN Deposition Precursor on a Silicon Substrate Precovered with a Layer of Titanium Carbonitride

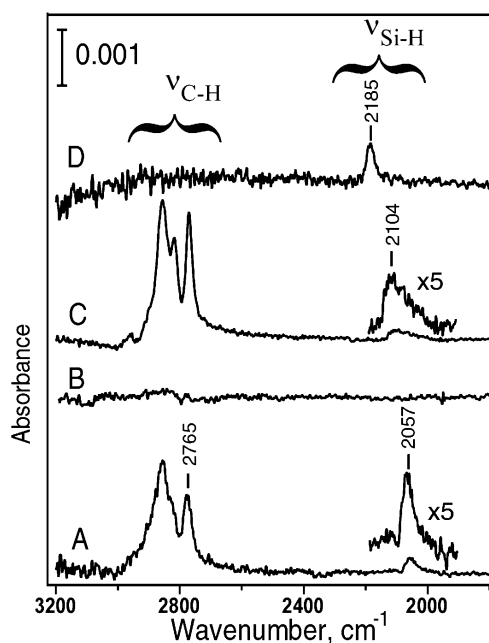
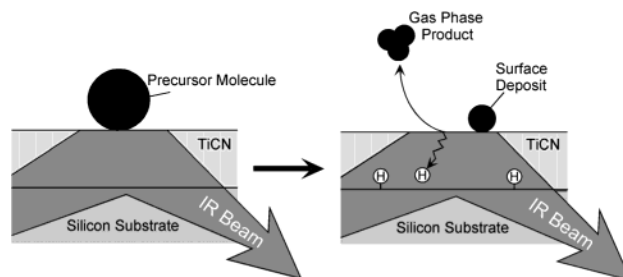


Figure 1. MIR FT-IR studies of TiCN at room temperature. (A) A saturated monolayer of TDMAT on a Si(100)-2×1 surface. (B) The sample from spectrum A briefly annealed to 850 K. (C) A saturated monolayer of TDMAT on a Si(100)-2×1 surface precovered with a 10-nm-thick TiCN layer. (D) A Si(100)-2×1 surface precovered with a 10-nm-thick TiCN layer exposed to 6000 L of H₂ with a hot W filament. TiCN-covered silicon surface is used as a background in spectra C and D.

The MIR FT-IR experiments were performed in a fully equipped ultra-high-vacuum chamber, which is coupled to a Fourier transform infrared spectrometer set up in a multiple internal reflection mode. The identity of the TDMAT and the absence of the decomposition products in the dosing gas were confirmed in situ by mass spectrometry and by analysis of the infrared spectrum of the multilayer TDMAT adsorbed at 95 K.

Spectrum A in Figure 1 corresponds to TDMAT adsorbed on a clean Si(100)-2×1 surface at room temperature. The characteristic

Bohlmann bands at 2765 cm^{-1} , corresponding to the interaction of the nitrogen lone pair orbital with the C–H σ -orbitals trans-periplanar to the lone pair, suggest that the adsorption product is similar in structure to the molecular TDMAT and that the majority of the $(\text{CH}_3)_2\text{N}^-$ groups are intact. It was also reported previously that the products of partial decomposition are manifested by the increased intensity of the C–H stretches as compared to the Bohlmann bands.¹³ Even though the exact identification of surface species is not possible on the basis of these spectra alone, it can be concluded that only a little decomposition to produce surface hydrogen occurs, as evidenced by the presence of a 2057 cm^{-1} absorption band corresponding to the Si–H stretch. As shown in spectrum B, surface hydrogen as well as all the other decomposition products that are visible in the IR region in our experimental setup can be removed by a brief thermal annealing to 850 K. Spectrum C in Figure 1 was obtained as follows: first, a clean and well-ordered Si(100)- 2×1 surface was exposed to 1000 L of TDMAT at 593 K ($320\text{ }^\circ\text{C}$) to produce a ~ 10 -nm-thick continuous and smooth film of TiCN (as confirmed by multiple analytical techniques described briefly above; this surface was used as a background in further infrared investigations),¹² and then the surface was cooled to room temperature and exposed to 1000 L of TDMAT to produce a saturated monolayer. Although the produced TiCN film is 10 nm thick, and a combination of surface analytical techniques suggest that there are no silicon atoms within this carbonitride layer, a vibrational feature at 2104 cm^{-1} indicates that, even at room temperature, hydrogen atoms from partial TDMAT decomposition easily reach the TiCN/Si interface. Since the background used in Figure 1C is the TiCN/Si as deposited at 593 K and cooled to room temperature, the 2104 cm^{-1} feature is specifically characteristic of room-temperature hydrogen diffusion toward the TiCN/Si interface. This hydrogen can also be removed by a brief annealing to 850 K. Since the absence of Si–H absorption bands in the spectrum of the titanium carbonitride film as deposited at 593 K was confirmed spectroscopically, the only reason for the presence of Si–H in spectrum C is the diffusion of hydrogen resulting from a partial decomposition of TDMAT on top of a 10-nm-thick carbonitride layer. Of course, this spectroscopic evidence does not show whether this diffusion process occurs directly through the titanium carbonitride film or through possible microscopic fractures not detected by our methods; however, the amount of hydrogen at this interface is similar to the amount of hydrogen on a Si(100)- 2×1 surface exposed directly to TDMAT at room temperature. It should also be noted that hydrogen diffusion along the Si(100)- 2×1 surface is negligibly slow at room temperature. Thus, together with the results of AES, TOF–SIMS, and AFM studies, the summary of the investigation shown in Figure 1 suggests that the diffusion process observed here spectroscopically indeed corresponds to diffusion *through* the film. These results show how powerful MIR FT-IR can be in studies of complex multilayered systems.

To confirm the hypothesis about hydrogen diffusion, atomic hydrogen was generated by catalytic dissociation of H_2 on a hot tungsten filament and dosed onto the silicon sample precovered with a 10-nm-thick TiCN layer. The spectroscopic result is presented in Figure 1D. The Si–H vibration is clearly observed at 2185 cm^{-1} , suggesting that atomic hydrogen produced by this method also easily diffuses toward the TiCN/Si interface.

The results of thermal desorption studies presented in Figure 2A show that recombinative desorption of hydrogen from a Si(100)- 2×1 surface occurs around 800 K if hydrogen is generated on a silicon surface by iodoethane dissociation followed by β -hydrogen elimination.¹⁴ Similar temperatures are reported for

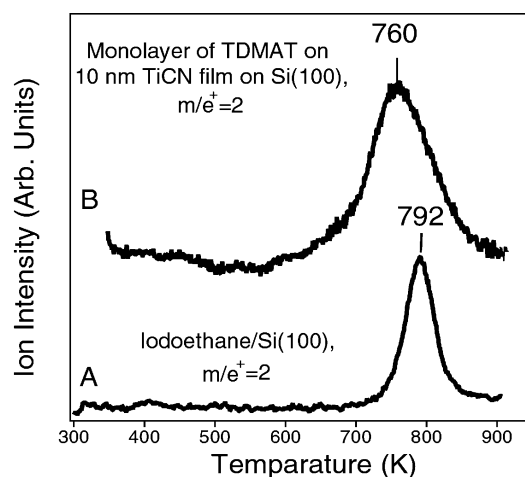


Figure 2. Thermal desorption studies of hydrogen desorption following $m/e^+ = 2$ from (A) a monolayer of iodoethane and (B) a 10-nm-thick TiCN film deposited at 593 K ($320\text{ }^\circ\text{C}$) and precovered with a monolayer of TDMAT. Heating rate, 2 K/s.

hydrogen desorption from a monohydride-covered Si(111) surface.¹⁵ When a 10-nm-thick titanium carbonitride film is produced on a Si(100)- 2×1 surface by exposure to TDMAT at 593 K ($320\text{ }^\circ\text{C}$), and then cooled back to room temperature and covered with a monolayer of TDMAT as a starting point, the thermal desorption trace in Figure 2B is observed.

The desorption temperature of hydrogen from this film correlates well with the observed breakdown temperatures for TiCN films in vacuum.^{11,11} While previous electrochemical analysis has shown that hydrogen diffusion is not responsible for degradation of TiN films,^{16,17} our results suggest that it is the chemical reaction that produces H_2 at the TiCN/Si interface that may cause the barrier layer to degrade.

Acknowledgment. A.V.T. gratefully acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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JA035026F