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Effect of film thickness and the presence of surface fluorine on the structure of a thin barrier film deposited from tetrakis-(dimethylamino)-titanium onto a Si(100)-2 × 1 substrate

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Abstract

The structure of a thin film deposited using tetrakis-(dimethylamino)-titanium ($Ti(N(CH_3)_2)_4$) as a precursor onto a Si(100)-2 × 1 substrate at ultra-high-vacuum conditions was investigated as a function of film thickness for the films of 20 and 145 nm in the presence of surface copper and fluorine produced by *in situ* dosing of a common copper deposition precursor, (hexafluoroacetylacetonate)Cu(vinyltrimethylsilane), (*hfac*)Cu (VTMS), and a hydrogenated form of the *hfac* ligand, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, *hfacH*. A combination of surface, depth-profiling, and microscopy analytical techniques suggests that the structure of the titanium carbonitride film depends profoundly on its thickness. While the composition of the film was relatively constant throughout its whole thickness, the nanometer-scale structure changed from amorphous at the top of a 145-nm-thick film, to having a significant amount of small (~5 nm) crystallites closer to the TiCN/Si interface. These studies also confirmed the absence of microfractures in the film prepared by this approach. The *ex situ* depth profiling investigation suggested that if (*hfac*)Cu(VTMS) is deposited on a TiCN-precovered silicon substrate and briefly annealed to 800 K, the film acts as a diffusion barrier for copper, while surface fluorine penetrates the film rather easily, resulting in fluorine that is distributed uniformly throughout the film.

Keywords: Transmission electron microscopy (TEM); X-ray photoelectron spectroscopy (XPS); Depth profiling; Titanium carbonitride

1. Introduction

One of the key components in modern semiconductor technology is a metal–semiconductor interface. It is desired for a number of reasons that this interface be sharp and thermally stable. However, to overcome the relatively easy interdiffusion of metal and semiconductor materials, and to improve the adhesion properties, barrier materials are usually used in manufacturing of these interfaces. While there are several materials used as diffusion barriers, titanium nitride, TiN, has a very attractive set of thermal and electrical properties [1–5]. Common procedures for chemical vapor deposition of titanium nitride include either dialkyl-amino derivatives ($Ti[NR_2]_4$, where R = Me, Et) [6–21], or $TiCl_4$ [1,22–25] used in combination with NH_3 and sometimes H_2; however, the latter poses severe problems associated with chlorine contamination and formation of NH_4Cl. To make the deposition process faster and more efficient, a variety of stimuli can be utilized, such as, for example, plasma-assisted [26], and photo-assisted CVD [27,28].

With all the approaches to titanium nitride deposition, a great deal of control has been achieved in manipulating the structure and purity of the films produced. For example, the amount of carbon in the films deposited from tetrakis-(dimethylamino)-titanium (TDMAT) and similar precursors can be reduced

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dramatically by adding N-containing compounds (e.g., NH_3) to the mixture [14,29]. At the same time, a reduction in carbon concentration is not always desirable. In fact, titanium carbonitride films, TiC_xN_y, have been shown to have a set of very attractive physical properties, including better conformal filling than titanium nitride [30–32].

The titanium carbonitride film deposited from TDMAT has been shown to have a stoichiometry of TiC_xN_y, with $x \sim y \sim 1$ [30,33]. The structure of the film has been elucidated by a number of analytical tools and was suggested to have most of the nitrogen atoms Ti-bound, while carbon atoms were either Ti-bound, or formed what is referred to as “organic carbon” [34]. Most importantly, the presence of small crystallites approximately 5 nm in diameter has been noticed in films with thickness of ~20 nm [30].

Here, a detailed structural study of titanium carbonitride thin films deposited on a Si(100) substrate was performed using a combination of *in situ* and *ex situ* surface analytical techniques. The *ex situ* studies were somewhat complicated by the fact the titanium carbonitride films are easily oxidized in ambient conditions [30,33]. However, for the structural studies presented here, the presence of oxygen can be taken into account.

An important question that is addressed in this paper is the diffusion of another key impurity element, fluorine, in titanium carbonitride films. These films have been shown to exhibit effective diffusion barrier properties with respect to copper [35] deposited from one of the most commonly used copper chemical vapor deposition precursors, (hexafluoroacetylacetonate)Cu(vinyltrimethylsilane), (*hfac*)Cu(VTMS). Copper deposition using this precursor molecule is a very efficient process, and titanium carbonitride films have been tested as diffusion barriers for copper. However, surface reaction of (*hfac*)Cu(VTMS), especially at the initial stages, leaves significant amounts of surface fluorine. Thus, it is important from a technical standpoint to understand whether titanium carbonitride films are efficient diffusion barriers with respect to fluorine, and from a fundamental standpoint, to understand how film structure affects the diffusion process in general.

2. Experimental details

Titanium carbonitride deposition, (*hfac*)Cu(VTMS) reaction, and preliminary Auger electron spectroscopy (AES) studies were performed in an ultra-high-vacuum chamber that has been described previously [36]. The Si(100) samples, polished on one side, were mounted on a manipulator with capabilities for heating and cooling from 135 to 1150 K. The samples were cleaned by the standard practice of sputtering with Ar^+ at room temperature, followed by annealing at 1150 K for 20 min, resulting in a clean and well-ordered surface as confirmed by AES and low-energy electron diffraction.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy measurements were performed *ex situ*. ToF-SIMS was performed on a computer-controlled instrument (TOF-SIMS IV, ION-TOF, Münster, Germany). Samples were loaded into the ToF-SIMS ultrahigh vacuum (UHV) analysis chamber through a vacuum sample transfer system. Depth profiles were collected by using a 1-keV Cs^+ sputter gun (for sample erosion) in conjunction with a 25-keV monoisotopic $^{69}Ga^+$primary ion beam (for sample analysis). The target current of the Cs^+ beam was ~5 nA, rastering over a $300 \times 300\ \mu m^2$ sample surface area for uniform ion exposure (current density $= 5.6\ \mu A\ cm^{-2}$). ToF-SIMS measurements performed by a Ga^+ analysis gun achieved high mass resolution ($m/\Delta m = 10{,}000$) using “bunched mode” of the primary ion source. The typical target current of the primary Ga^+ beam in bunched mode was ~1 pA with a prebunched pulse width of 20 ns and a sub-ps pulse width at the surface after bunching. The Ga^+ analysis beam (60–600 nm diameter, depending on the objectives of the analysis) was directed to the center of the sputter crater formed by the Cs^+ erosion gun.

XPS analysis was performed on an ESCALab 220i-XL electron spectrometer (VG Scientific, East Grinstead, UK) with a monochromatic aluminum Kα ($h\nu = 1486.7$ eV) X-ray source. Typical operating conditions for the X-ray source employed a 400-μm nominal X-ray spot size (full width at half maximum) operating at 15 kV, 8.9 mA (134 W) for both survey and high-resolution spectra. A 2-μm-thick aluminum window was used to isolate the X-ray monochromator chamber from the sample analysis chamber to prevent high-energy electrons from impinging on the sample and possibly altering the native surface chemistry. Survey spectra, from 0- to 1200-eV binding energy, were collected at 100-eV pass energy, resulting in an energy resolution of ~1.0 eV, with a dwell time of 100 ms per point, and a total of two scans (averaged). High-resolution spectra were collected at a pass energy of 20 eV, resulting in an energy resolution of ~0.1 eV, with a dwell time of 100 ms per data point, and a total of 10–15 scans (averaged) in the respective binding energy ranges. The operating pressure of the spectrometer was typically in the 10^{-8} Pa range, with a system base pressure of 2×10^{-8} Pa. Data processing was performed using CasaXPS software (London, UK, version 2.2.11). The XPS spectra were fitted using line-shapes of 70% Gaussian–30% Lorentzian product functions unless otherwise specified.

Transmission electron microscopy (TEM) was performed to reveal the structural details of the thin film. Cross-sectional TEM thin foils were prepared by gluing two pieces of the sample face to face with M-Bond 610 Adhesive, grinding the block perpendicular to the interface on both sides to ~10 μm thick with a Gatan 656 Dimple Grinder, and then ion-milling the section on a Gatan 600 Dual Ion Mill to obtain electron beam transparent regions across the interface. TEM characterization was conducted using a JEOL JEM-2010F field emission transmission electron microscope operating at 200 kV, and images were collected with a Gatan multi-scan CCD camera in a Gatan Image Filter (GIF) unit.

Argon (99.9999%, Matheson) was used without further purification for sample cleaning through sputtering. Tetrakis-(dimethylamino)-titanium, TDMAT, (99%, First Reaction) and (*hfac*)Cu(VTMS), (CupraSelect, Air Products) were transferred into a glass vial connected via a glass-to-metal transition with a stainless steel bellows valve in a nitrogen glove box to avoid oxidation processes in air. 1,1,1,5,5,5-hexafluoro-2,4-pentane-