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Research Letter

Transparent and passive Ta–Si–N thin films barrier layer

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Abstract

Amorphous ternary Tantalum Silicon Nitride (Ta–Si–N) is an oxidation/diffusion barrier layer for microelectronic devices. The transparency of Ta–Si–N with increased nitrogen content in the wavelength range 200–1700 nm was investigated. Good transmittance was obtained with low amount of nitrogen in the layer. Passivity of Ta–Si–N to the thermochromic property of VO_2 films and the high oxidation temperature for vanadium are reported. The relative nitrogen content in each layer was determined with Energy-Dispersive x-ray Spectroscopy. Both the transparency and passivity Ta–Si–N made it a suitable candidate for opto-electronic device applications.

Introduction

There have been numerous studies on the diffusion barrier characteristics of ternary system TM–Si–N (TM is Transition Metal), especially in VLS Microelectronic fabrications.[1–6] The low diffusivity and miscibility of Cu with tantalum has encouraged active research on Ta–Si–N as barrier layer for Cu diffusion in VLSI interconnects.[7–14] Ta–Si–N thin film is a hard material, and it is thermally, chemically, and mechanically stable over a wide range of temperatures. The property stability stems from the refractory property of the transition metals. The Ta–Si–N films could be obtained by means of reactive co-sputtering of two separate Ta and Si targets or a single target containing Ta and Si ($TaSi_2$ or Ta_5Si_3) at various nitrogen levels in the Argon sputtering gas.[15–18]

More recently, other materials and different deposition methods have been explored for barrier layer of copper interconnects.[19] Ultra-thin layers of Platinum Group Elements (PGEs)-based materials,[20] Two-Dimensional (2D) materials,[21–23] and Self-Assembled Molecular Layers[24] have shown promises to prevent copper diffusion. These materials and methods have their own issues.

Apart from the application of Ta–Si–N as Cu diffusion barrier layer for microelectronics interconnect fabrications because the layer is amorphous as-deposited and stays amorphous above 1000°C for few hours,[25–29] the lack of grain boundaries that could serve as diffusion path for mass transport of foreign elements such as oxygen does not exist. It is, therefore, a good oxidation barrier layer for contact metallization of wide band-gap semiconductor devices for high power, elevated temperature, and harsh environment applications.[6] Ta–Si–N alloy may be used as well for micro-electromechanical systems (MEMS) where it offers a novel combination of thermally adjustable stress, mechanical characteristics, and selectivity in etching.[30]

The amount of nitrogen in the Ta–Si–N layer affects both the sheet resistance and the barrier layer effectiveness of the material. In the applications mentioned above, trade-offs between the films sheet resistance and the barrier layer effectiveness, as dictated by the amount of nitrogen in the layer, are crucial.

In this work, the transparency of Ta–Si–N layer on fused quartz substrates with the amount of nitrogen is reported. The optical transparency and passivity of the layer are demonstrated by comparing the thermochromic characteristic of VO_2 on quartz with sandwiched VO_2 layer between layers of Ta–Si–N layers on quartz substrate.

Results and discussions

Results

The color of Ta–Si–N samples on quartz goes from metallic gray (0–3% nitrogen flow rate) to light greenish yellow (above 5% nitrogen flow rate). The percent increase in the nitrogen content of the layers was determined from the EDS data. Data show the nitrogen content in the layer increases with percentage flow rate of nitrogen in the sputtering gas and then saturates as shown in Fig. 1(a). The relative Si content in the layer decreases as the nitrogen content increases. Figure 1(b) shows that the sheet resistance of Ta–Si–N layer increases exponentially with percentage increase in nitrogen content. After the initial surge, the sheet resistance starts to saturate as the percentage nitrogen begin to saturate.

Figure 2(a) shows the transmittance spectra (from 200 to 1600 nm) of Ta–Si–N samples at room temperature. The spectra showed increase transmittance with increased nitrogen content in the thin films. The transparency saturates just as the nitrogen contents in the Ta–Si–N saturates with nitrogen flow rate. The saturation of the transmittance is shown in Fig. 2(b)

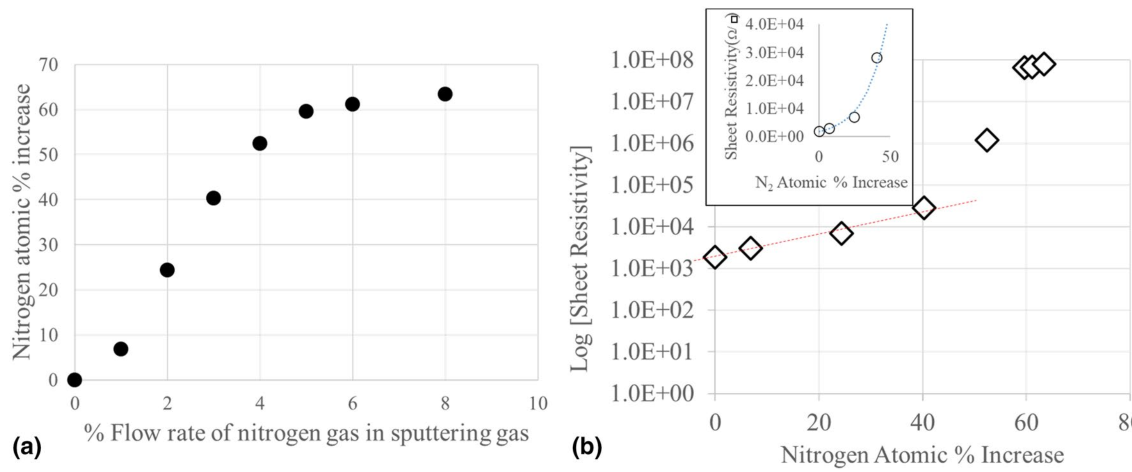

Figure 1. (a) EDS atomic percentage increase of nitrogen content in samples with different percentages of nitrogen gas by flow rate in sputtering gas. (b) Log of sheet resistivity versus EDS atomic percent of nitrogen in samples—the inset is the first four data points that indicated exponential growth of the sheet resistivity with increased nitrogen in the layers.

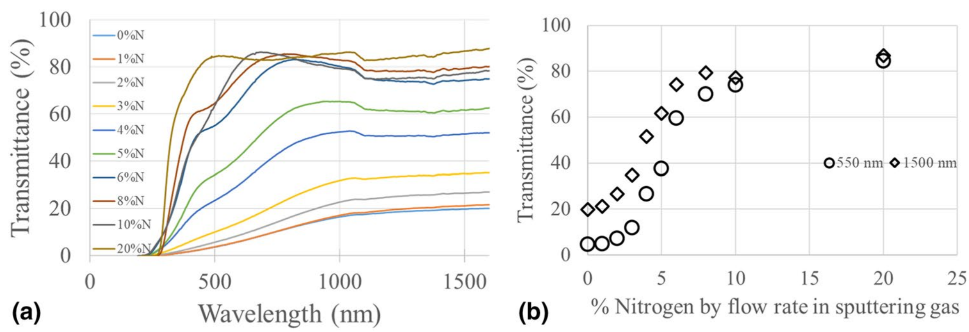

Figure 2. (a) Transmittance spectra of samples with different percentage of nitrogen gas by flow rate in sputtering gas. (b) Transmittance at 550 nm and 1500 nm for samples with different percentage of nitrogen gas by flow rate in sputtering gas.

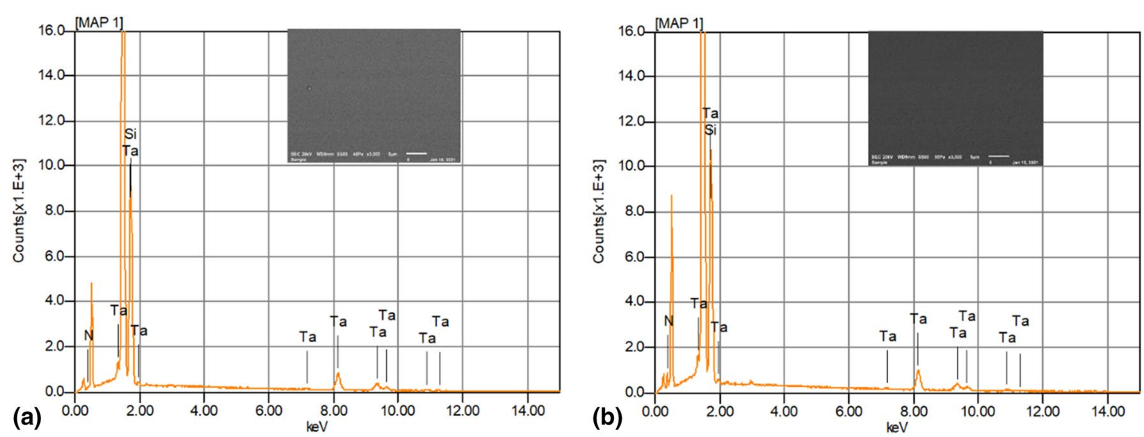

Figure 3. EDS data showing the composition of Ta–Si–N samples on quartz substrate with inset SEM images. (a) Sample with unintended nitrogen content (b) Sample with 5% nitrogen by flow rate in sputtering gas.

at wavelengths of 550 nm and 1500 nm. The thicknesses of the layers, as measured with a contact profiler, did not change significantly with nitrogen content. The EDS spectra for 0% and 5% nitrogen flow rates are shown in Fig. 3 (a) and (b) respectively. Atomic percentages of constituent elements were obtained from the corresponding x-ray energy peaks. The insets in Fig. 3 are Scanning Electron Microscope images, they indicate very smooth surfaces of the Ta–Si–N layers.

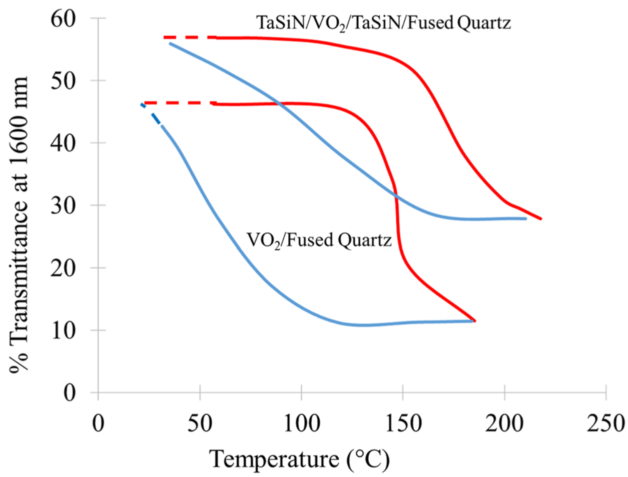

Figure 4. Plot of Transmittance at 1600 nm versus Temperature for naked VO_2 layer on quartz substrate and sandwiched VO_2 layer in Ta–Si–N layers on quartz substrate.

Figure 4 shows the transmittance versus temperature of unprotected VO_2 layer and VO_2 layer sandwiched by Ta–Si–N layers on quartz substrates. Similar reversible thermochromic properties of VO_2, "hysteresis like" curves, were obtained for both samples.

Discussions

The Ta–Si–N layer is not a compound, it is a mixed composite of Ta–Si, Ta–N, and Si–N compounds. It is more transparent because of the high nitridation of Ta and Si that lead to less optically dense and diluted Ta–Si–N layer. The layers become more transparent in the wavelengths range inspected. The excellent oxidation and diffusion barrier characteristics of Ta–Si–N for VLSI microelectronic contact metallization are well known in the literatures. What has not been reported is the transparency of the layer with increased nitrogen content. Transparent and excellent barrier characteristics would find applications in opto-electronic industries.

However, for high transparency (> 70% transmittance) applications, nitrogen flow rate higher than 5% is required but the associated sheet resistance of the layer would be very high. A trade-off between transparency and sheet resistance is necessary, based on intended application.

Magnetron-sputtered Ta–Si–N thin films showed optical passivity on VO_2 layer. The unprotected VO_2 thin films on quartz substrate and the sandwiched VO_2 by Ta–Si–N layers showed the expected thermochromic transition that is reversible, as shown in Fig. 4, though the transition occurred for both samples at higher temperatures than the expected 68°C transition temperature for VO_2. The higher transition temperatures may be related to samples processing method that might have introduced higher strains in the VO_2 layers. Both samples were affected by the processing method and their transmittance–temperature curves are similar. However, the curves indicated that Ta–Si–N layers enveloping VO_2 did not degrade or impede the transition characteristics of VO_2. The Ta–Si–N layers enhanced the transmittance, showing anti-reflective property that is due to the layers' relative indices of refractions. Based on the way the sandwiched sample was made, vanadium metal layer sputtered at room temperature on Ta–Si–N-coated quartz glass was oxidized in N_2 and O_2 gas at 500°C for 4 h. Ta–Si–N layer did not mix with the vanadium layer during oxidation, and neither was it oxidized. Previous Scanning Tunneling Electron Microscope (STEM) images of the interface between VO_2 and Ta–Si–N layers have been very stable. A transparent, oxidation/diffusion barrier layer that can retain its characteristics at elevated temperature for a long period of time would enable fabrication flexibility that could benefit opto-electronic device fabrication process.

Conclusions

The transparency of Ta–Si–N on quartz substrate was investigated for possible application as oxidation/diffusion barrier layer on opto-electronic materials and devices. The transparency of sputtered Ta–Si layer increases with the increase in nitrogen content that causes nitridation of Ta and Si that results in the decrease of the optical density of the layer. The transmittance above 70% was observed for samples with more than 5% nitrogen content by flow rate, at both visible and near-IR wavelengths. The price paid for the increased transparency of Ta–Si–N is the dramatic increase in the sheet resistivity of the layer. The optical and electrical characteristics of VO_2 layer sandwiched by Ta–Si–N layers showed that the thermochromic property of the VO_2 layer is preserved and is comparable to the samples with no Ta–Si–N covering. The high passivity of the Ta–Si–N layers, despite the harsh oxidation conditions of the vanadium layer, indicates possible application of transparent Ta–Si–N as protective oxidation/diffusion barrier layer for opto-electronic devices at elevated temperatures.

Experiments

Deposition of Ta–Si–N thin films

Ta–Si–N thin films were deposited on clean fused quartz substrates by magnetron sputtering of 99.5% pure $TaSi_2$ target in Ar or Ar + N_2 gas mixtures. 0–20% of nitrogen by flow rate in the gas mixture [% flow rate of nitrogen = $\frac{N2}{[Ar+N2]}$ × 100]. The base pressure in the sputtering chamber was about 10^{-7} torr and the sputtering pressure was 10 millitorr for all the samples. The depositions were done with 100-Watt RF power.

Sandwiched VO_2 sample

Sandwiched VO_2 sample was fabricated on clean fused quartz substrate, Quartz/Ta–Si–N/VO_2/Ta–Si–N. Transparent

Ta–Si–N was deposited as discussed above with 20% of Nitrogen by flow rate in the sputtering gas on substrates (1.0 cm × 1.0 cm) at room temperature. Then, 99.5% pure vanadium was deposited on 0.8 cm × 0.8 cm area of the Quartz/Ta–Si–N sample. The Quartz/Ta–Si–N/V layer was annealed in quartz tube furnace at 500°C, 800 millitorr pressure in nitrogen and oxygen gases for 4 h. Gold contacts were subsequently deposited at the corners by sputtering as well. After the thermal oxidation and gold contacts metallization of VO_2 layer, Ta–Si–N cover layer was sputtered as the cap layer.

Optical and electrical properties

The transmittance and reflectance of Ta–Si–N samples on quartz were simultaneously measured at room temperature for samples with different amount of nitrogen. The filmetrics instrument measured the transmittance and reflectance spectra from 200 to 1700 nm. For the sandwiched VO_2 sample, to observe the impacts of Ta–Si–N layers on the well-known thermochromic transition, the spectra were measured as a function of temperature.

Van der Pauw 4-point probe method was used to measure the sheet resistance of the Ta–Si–N samples and the sandwiched VO_2 sample. The sheet resistance of the sandwiched VO_2 sample was measured as a function of temperature to observe the transition temperature.

Surface morphology and atomic composition

JEOL JSM-6010Plus/LA analytical scanning electron microscope was used to acquire the surface morphology images of Ta–Si–N samples and their atomic compositions in 50 Pa vacuum pressure mode. KLA Tencor P-7 contact profiler was used to determine the thickness of the samples. The thickness of VO_2 layer was measured to be 85 nm and Ta–Si–N was 130 nm.

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Declarations

Conflict of interest

None to be reported.

Supplementary Information

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