

Thermal oxidation of reactively sputtered amorphous $W_{80}N_{20}$ films

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The oxidation behavior of reactively sputtered amorphous tungsten nitride of composition $W_{80}N_{20}$ was investigated in dry and wet oxidizing ambient in the temperature range of 450 °C–575 °C. A single WO_3 oxide phase is observed. The growth of the oxide follows a parabolic time dependence which is attributed to a process controlled by the diffusivity of the oxidant in the oxide. The oxidation process is thermally activated with an activation energy of 2.5 ± 0.05 eV for dry ambient and 2.35 ± 0.05 eV for wet ambient. The pre-exponential factor of the reaction constant for dry ambient is 1.1×10^{21} Å²/min; that for wet ambient is only about 10 times less and is equal to 1.3×10^{20} Å²/min.

INTRODUCTION

Tungsten nitride thin films have been studied as diffusion barriers in various metallization systems for applications to Si and GaAs.¹⁻³ Depending on the nitrogen concentration, reactively sputtered $W_{1-x}N_x$ could be either amorphous or polycrystalline.^{4,5} It has been found that amorphous $W_{1-x}N_x$ is a better diffusion barrier than the polycrystalline forms.^{1-3,6} Although this superior performance could not be positively attributed yet to the lack of grain boundaries of the amorphous form because the atomic composition changes together with structure, it is known that diffusion barriers often fail through grain boundary diffusion.

In oxidizing ambients, tungsten metal turns into oxides of which there are several forms depending on the oxygen content.⁷ Of these oxides, the form WO_3 has unique electrical and optical properties.^{8,9} WO_3 is insulating, but becomes conducting when there are oxygen vacancies. It is also dichromic and ferroelectric. A better understanding of its properties could lead to applications in integrated capacitors and in optical interconnects.

At elevated temperatures in oxidizing ambients, tungsten nitride transforms to tungsten oxides. This can be understood from a comparison of the heats of formation of tungsten nitride and of the various forms of tungsten oxides (Table I). In an ambient rich in oxygen, W metal is transformed to WO_3 . Which oxide is formed upon thermal oxidation of tungsten nitride and according to what kinetics were the goals pursued by this work. Apart from assessing the possible applications of tungsten nitride in an oxidizing ambient, this study of tungsten oxides growth is interesting from the point of view of materials properties. With tungsten being considered as a candidate material for advanced interconnects, the use of its nitrides and oxides as components of metallization systems greatly simplifies manufacturing processes.

In this work, we study the oxidation kinetics of amorphous $W_{80}N_{20}$. The oxidation temperatures between 450 °C and 575 °C were chosen to be in the range of interest for diffusion barrier application, at the same time staying below the recrystallization temperature of the amorphous nitride which was determined to be around 620 °C.⁴ The ki-

netics of the oxidation process is derived from 2 MeV $^4He^+$ backscattering spectra.

EXPERIMENTAL PROCEDURES

$\langle 111 \rangle$ oriented *n*-type silicon with resistivity around 5 mΩcm was used to make the SiO_2 substrates. The tungsten nitride films were deposited on these substrates by reactive rf magnetron sputtering using a planar W cathode of 7.5 cm diam. The substrate holder was placed about 7 cm below the target and was neither cooled nor heated externally. The background pressure was 5×10^{-7} Torr or better prior to deposition. The sputtering gas was a mixture of argon and nitrogen. The flow ratio of Ar to N and the total gas pressure were adjusted by mass-flow controllers and monitored with a capacitive manometer in a feedback loop. The total gas pressure is kept at 10 mTorr and the total gas flow is around 66 sccm. The forward sputtering power was 400 W and the ratio of N to total gas flow around 8%.

The structure of the deposited films was shown by Read camera pictures to be x-ray amorphous. The composition of the as-deposited films as determined from the height ratio of backscattering spectrometry signals of films deposited in the same run on carbon substrates is shown to be $W_{80}N_{20}$. This result is in agreement with previous work.^{4,5}

The composition of the oxidized layers was determined from the height ratios of signals corresponding to the oxidized and unoxidized layers, respectively. The kinetics of growth of the films was measured by 2 MeV $^4He^+$ backscattering spectrometry. To determine the molecular density of the nitride and of the resulting oxide, the thickness of the films was measured mechanically with a Sloan-Dektak stylus profilometer.

TABLE I. Heats of formation for tungsten nitride and tungsten oxides according to Goldschmidt (see Ref. 7).

	Heats of Formation
W_2N	– 17 kcal/mole
WO_2	– 135 kcal/mole
WO_3	– 200 kcal/mole

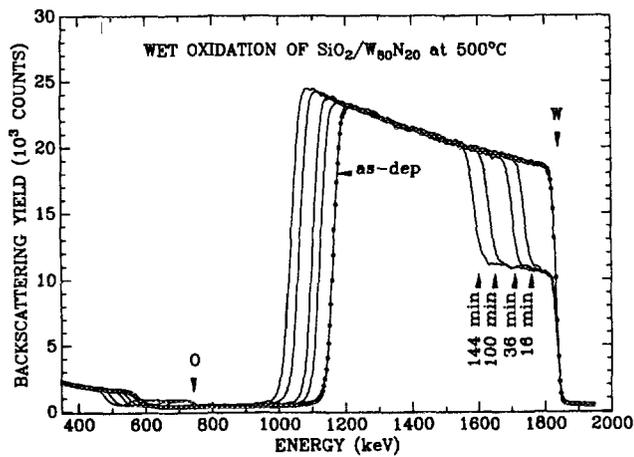


FIG. 1. 2.0 MeV $^4\text{He}^+$ normal incidence backscattering spectra of a series of similar $(\text{Si})/\text{SiO}_2/\text{W}_{80}\text{N}_{20}$ structures as-deposited and oxidized in a wet ambient at 500 °C for various times. The scattering angle is 170°.

The deposited nitride films were oxidized in an open-ended quartz tube furnace with an oxygen gas flow of 100 cm^3/min . The wet oxidation was carried out in the same furnace by bubbling the oxygen through a bottle of deionized water maintained at 97 °C prior to entering the furnace through feeding conduits kept at 106 °C. The oxidation temperatures range from 450 °C to 575 °C. All temperature measurements are regulated to within ± 2 °C.

RESULTS AND DISCUSSION

Figure 1 shows typical backscattering spectra of five similar samples, as-deposited and oxidized at 500 °C for various times in a wet ambient. One observes after annealing an oxide layer on top of the nitride layer. The oxygen signal can be clearly seen. The well-defined edges indicate that the interface between the oxide and nitride is sharp and that the oxide layer is relatively uniform in depth. The composition of the oxide was determined, in all cases in this work, to be WO_3 to within an uncertainty of 5%. X-ray diffraction analysis established that monoclinic WO_3 was present in the annealed sample. The diffraction rings are incomplete (nonuniform darkening) indicating that the oxide grains have a preferred orientation. The remaining tungsten nitride layer underneath the oxide remains amorphous after the oxidation.

To determine the thickness of the various layers from backscattering spectra, one needs to know the molecular density of the nitride and of the oxide. For the nitride, this was obtained by measuring the thickness of a given layer with a Sloan–Dektak stylus profilometer. The energy loss due to that layer is obtained from its backscattering spectrum. From these two informations, we derive the molecular density.¹⁰ For the oxide, the total thickness of a partially oxidized nitride film is measured by profilometer. Since the molecular density of the nitride is now known, the thickness of the nitride layer underneath the oxide can be obtained from a backscattering spectrum of the partially oxidized film. The thickness of the oxide layer is then obtained as the difference between the total thickness of the

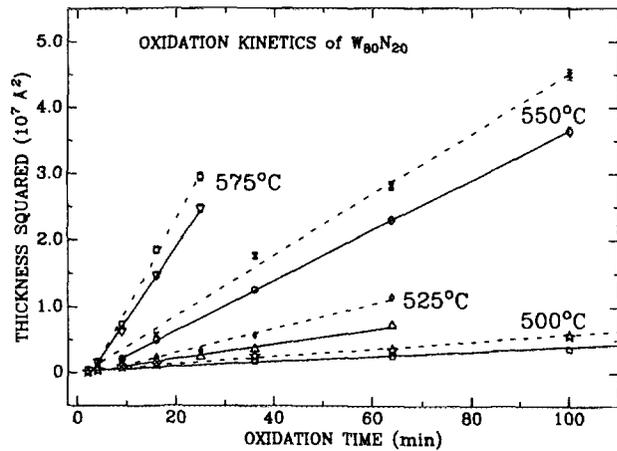


FIG. 2. Plot of the oxide thickness squared vs oxidation time at various temperatures. The solid lines are linear fits to the data points obtained in a dry ambient. The dashed lines are linear fits to the data points obtained in a wet ambient.

partially oxidized film measured by profilometer and the computed thickness of the nitride layer underneath the oxide. With the thickness of the oxide layer now known and the energy loss due to that oxide layer measured on the backscattering spectrum, the molecular density of the oxide is derived in the same way as for the nitride. The densities of $\text{W}_{80}\text{N}_{20}$ and WO_3 were determined to be 7×10^{22} molecules of $\text{W}_{0.8}\text{N}_{0.2}$ and 2×10^{22} molecules of WO_3 per cm^3 , respectively, to within $\pm 10\%$. The density of the nitride is in agreement with previous results.⁴ The density of the oxide thus obtained is within 10% of published results on bulk WO_3 .^{11,12}

The kinetics of the oxide growth at a given temperature was investigated by measuring the thickness of the oxide layers with backscattering spectrometry using the oxide molecular density value obtained as mentioned above, after oxidation of similar samples for various times. Figure 1 shows the gradual increase of the oxide thickness with oxidation time. The as-deposited $\text{W}_{80}\text{N}_{20}$ film thickness is about 5000 Å. Figure 2 shows the plot of the square of the oxide thickness as a function of time in a dry (solid lines) and wet oxidizing ambient (dashed lines). The good fit of the data points with straight lines indicate a relationship of the form

$$d^2 = Kt,$$

where d is the oxide thickness, t the oxidation time and K the parabolic rate constant of oxidation. At the temperature of 450 °C, however, the growth kinetics seems to differ from that at higher temperatures. A parabolic growth is no longer observed. Figure 3 shows the plot of the logarithm of the oxide thickness versus the logarithm of the oxidation time at 450 °C in a dry ambient. A slope of 0.26 ± 0.01 is obtained for the linear fit shown. This indicates that a different growth mechanism is involved at lower temperatures, a situation which has already been observed for tantalum nitride films.¹³ Further work in the temperature range below 450 °C is needed to clarify this point.

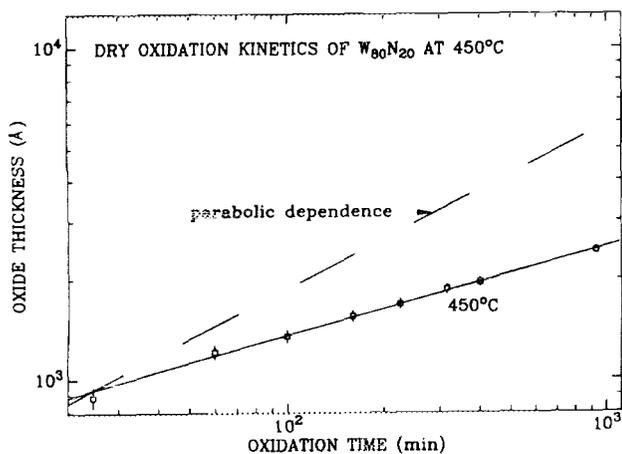


FIG. 3. Plot of the oxide thickness versus oxidation time at 450 °C in a dry ambient. The solid line is the linear fit to the data points with a slope of 0.26 ± 0.01 . The dashed line represents a parabolic dependence.

In Fig. 4, the values of the parabolic rate constant K are plotted on a logarithmic scale as a function of reciprocal oxidation temperature. In the temperature range where the parabolic relation between d and t holds, we obtain a good linear fit yielding an exponential Arrhenius relationship of the form

$$K = K_0 \exp(-E_a/kT),$$

where K_0 is the temperature-independent pre-exponential factor, E_a the thermal activation energy associated with the parabolic oxidation process, k the Boltzmann constant and T the oxidation temperature in degrees Kelvin. The values of K_0 and E_a derived from the straight lines of Fig. 4 are presented in Table II. We note that the oxidized layer thickness at a given temperature is only about 50% larger in a wet ambient than in a dry ambient. This is to be compared to the order of magnitude difference observed for the case of titanium nitride.¹⁴

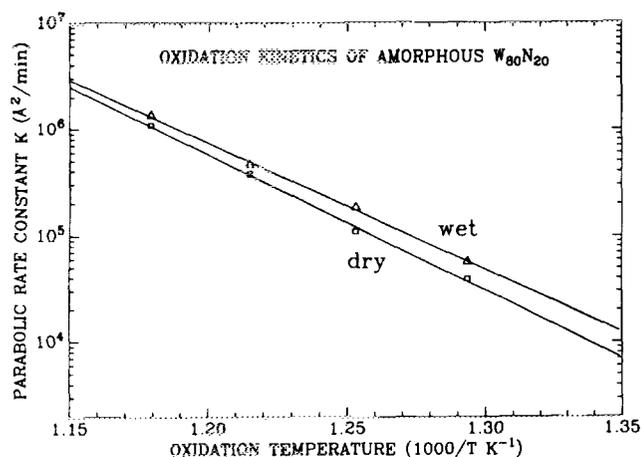


FIG. 4. Logarithmic plot of the parabolic rate constant K vs reciprocal oxidation temperature in the temperature range where the relation $d^2 = Kt$ holds. The solid lines are linear fits to the data points in dry and wet ambients.

TABLE II. Constants E_a and K_0 related to the parabolic oxidation rate for $W_{80}N_{20}$.

Ambient	Activation Energy E_a (eV)	Pre-exponential Factor K_0 ($\text{\AA}^2/\text{min}$)
Dry	2.5 ± 0.05	1.1×10^{21}
Wet	2.35 ± 0.05	1.3×10^{20}

The resistivity of the as-deposited amorphous $W_{80}N_{20}$ as measured by four point probe is $180 \mu\Omega\text{cm}$ and agrees with previous results.^{1,4,5} The resistivity of the oxidized layer resulting from the oxidation of the nitride was found to be very high, beyond measurement with four-point probe setups. This is also in agreement with the known insulating property of WO_3 .

The observed parabolic time dependence of the oxide growth in the temperature range 500 °C–575 °C suggests a diffusion-limited mechanism. As discussed by Suni *et al.*¹⁴ for the case of TiN, we surmise that the dominant diffusing species is oxygen. While water seems to play a catalytic role in the oxidation of TiN leading to a large difference between wet and dry ambients, such an effect is much less important with amorphous tungsten nitride.

CONCLUSION

In many instances of transition metal nitrides,^{14–17} the kinetics of growth of the corresponding metal oxides in a thermal oxidizing ambient is diffusion-limited leading to a parabolic time dependence. This also holds true for amorphous $W_{80}N_{20}$ in the temperature range of 500 °C–575 °C. A study of the kinetics in a lower temperature range is being planned and is most interesting with a quartic law dependence at 450 °C. Tungsten nitride is a material with different structures depending on its N content. The resulting oxides could also differ in their structures. Thus they could serve as vehicles for testing diffusivity properties in these various structures. Such a study is being planned.

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