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2

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X-RAY CHARACTERIZATION OF OXIDIZED TANTALUM NITRIDE

R. L. MaSaitis and R. L. Opila
AT&T Bell Laboratories
600 Mountain Ave
Murray Hill, NJ 07974

A. O. Ibidunni
AT&T Bell Laboratories
1600 Osgood Street
North Andover, MA 01845

A. J. Davenport and H. S. Isaacs
Dept. of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

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Sputter deposited non-stoichiometric tantalum nitride films are oxidized in air between 200 and 500 °C to form a passive film. The oxidized films have been studied with x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption near edge spectroscopy (EXAFS). Films exposed to KOH formed a non-protective surface layer identified in low angle XANES and EXAFS as $KTaO_3$. Auger electron and x-ray photoelectron spectroscopies were also used to characterize these films.

INTRODUCTION

The oxidation of polycrystalline, metallic tantalum is limited by the formation of a passivating layer of Ta_2O_5 [1,2]. As exposure to O_2 at high temperatures (>400 °C) proceeds, the thickness of the Ta_2O_5 increases. In addition, oxygen diffuses into the underlying bulk metal. After the limit of oxygen solubility is reached, metastable Ta suboxides precipitate.

The oxidation of thin films of amorphous tantalum nitride (actually $TaN_{0.3}$) has also been studied [3,4,5]. The oxidation of these films is similar to the oxidation of metallic, polycrystalline Ta in that a passive Ta_2O_5 film forms. However, directly beneath the passive film another layer develops that contains Ta, O, and N. This layer was thought to be an oxynitride [4,5], but has recently been shown to be a mixture of Ta_2O_5 and non-stoichiometric tantalum nitride. The precipitation of stoichiometric Ta_2O_5 occurs with the amorphous nitride films but not the metal because the N can be displaced by O leading to the formation of Ta_2N nearby. Since such a replacement is not possible in polycrystalline Ta, nucleation of the oxide does not occur as readily.

Recent work on thin films of tantalum nitride has shown that the oxidation protection offered by the passive Ta_2O_5 is destroyed on exposure to KOH [4]. The films lose their characteristic gray color and become transparent, suggesting that the entire layer is oxidized to Ta_2O_5. However, Auger spectroscopy showed that potassium was incorporated into the surface layer and formed a compound that is insoluble in water. The thickness of the surface oxide and the amount of oxygen in the bulk increased slightly.

The following model was invoked to explain these results. The KOH converts the Ta_2O_5 to $KTaO_3$. $KTaO_3$ is insoluble in water and presumably forms a layer that allows more rapid O_2 diffusion than Ta_2O_5, leading to oxidation of the underlying nitride. Instead of forming a new passive film, Ta_2O_5 nucleates around domains of tantalum nitride, as seen for air oxidation of these nitride films. If the domains of conductive tantalum nitride are not connected to each other and are smaller than the wavelength of visible light, these films will appear transparent. The evidence for the presence of $KTaO_3$ was entirely circumstantial. Previous work with electron-induced Auger electron spectroscopy and x-ray photoelectron spectroscopy showed that $KTaO_3$, Ta_2O_5, and the putative $KTaO_3$ surface layer had identical chemical shifts for both Ta and O. Thus, while these compounds could be distinguished from metallic Ta or amorphous or crystalline tantalum nitrides, they were mutually indistinguishable.

The work reported here was initiated because x-ray absorption spectroscopy is more sensitive to the local environment of the Ta atom than these electron spectroscopies. This is particularly important in the study of these amorphous films which lack the long range order found in crystalline materials. X-ray absorption near edge spectroscopy (XANES) can probe the electronic structure about the central Ta atom and extended x-ray absorption fine structure (EXAFS) can be used to study the local atomic order.

EXPERIMENTAL

Tantalum nitride films were deposited on alumina substrates by reactive d-c sputtering from a 99.99% tantalum target in a mixed argon-nitrogen atmosphere. The film thickness was controlled by the sputtering power and the nitrogen concentration in the films was a function of the nitrogen/argon ratio and the sputtering power. Films were approximately 700Å thick. The resultant films were non-stoichiometric TaN_y, with $y \approx 0.3$. Polycrystalline films of this composition are expected to have two phases, a Ta rich phase containing dissolved N, and a Ta_2N phase [6]. Thus, these films will be designated as

$Ta_{2+x}N$ in this paper. X-ray diffraction showed that these films are amorphous. $Ta_{2+x}N$ films deposited on Al_2O_3 substrates and oxidized in air at 350 °C for 1 hour were dipped in 1M KOH at 80 °C for 60 min.

The X-11A Beamline at the National Synchrotron Light Source at Brookhaven National Laboratory was used to perform XANES and EXAFS. The Ta L_{III} absorption edge (E_0 = 9881.1eV) was measured for stoichiometric TaN, Ta_2O_5, and $KTaO_3$ powders (>99.9% purity) in conventional transmission geometry. Sputtered $Ta_{2+x}N$ films, as deposited, oxidized in air at 475 °C for 55 minutes, and reacted with KOH as described above were measured in fluorescence using low incident angles, as described previously [7]. The as-deposited and air oxidized films showed evidence of W contamination by the L_{III} edge at 10207 eV.

RESULTS AND DISCUSSION

Because EXAFS and XANES are sensitive to the valency state and atomic structure in the immediate vicinity of the probed atom, they were used to distinguish $KTaO_3$ from Ta_2O_5. The normalized XANES results are shown in Figure 1 for the film exposed to KOH and the standards for TaN, Ta_2O_5, and $KTaO_3$. Both the KOH treated film and the powdered $KTaO_3$ spectra have a doublet with a separation of 4 eV, unlike those seen for any of the other standards or films studied here. Since the L_{III} transition probes the empty 5d levels with electrons that originate in the 2p shell, the shape of the L_{III} edge reflects the effects of the crystal field on the 5d orbitals. The doublet in the L_{III} edge has been seen previously for Ta substituted into TiO_2 rutile solid solutions [8,9]. In this case, the octahedral crystal field splitting of the 5d levels is approximately 6 eV. For $\beta-Ta_2O_5$, which is orthorhombic, the Ta 5d levels do not experience a symmetric ligand field, so the 5-fold degeneracy will be removed. Consequently, instead of a doublet, an unresolved pentuplet results for this compound. Thus, the observed XANES spectrum for the film is consistent with the spectrum for $KTaO_3$.

Attempts to fit the spectrum of the KOH treated film as a linear combination of the standard TaN, Ta_2O_5, and $KTaO_3$ spectra failed because the width of L_{III} line for the film was too great. There are several reasons for this width. The film is disordered, so each component is inhomogeneously broadened, as shown below by EXAFS. The spectrum of each film, as-deposited tantalum nitride, air oxidized tantalum nitride, and treated with KOH, was broadened in comparison with the standard compound. It is likely that some fraction of this broadening was due to self-absorption of the incident beam in the film. The self-absorption decreases the penetration depth of x-rays into the sample, thus suppressing the fluorescence signal in those parts of the spectrum where the absorption coefficient is greatest [10]. As a result the shoulders of the absorption will be enhanced relative to the peak, i. e., the peak will be broadened. This broadening was not seen for the standards because these samples were finely dispersed powders measured in transmission.

The EXAFS results shown in Figure 2 corroborate the XANES results. These Fourier transforms have been generated after removing the background and filtering. The features seen at approximately 1.5, 3, and 3.5 Å in the transforms for $KTaO_3$ powders and the KOH treated film correspond to scattering from the first-shell oxygen and potassium atoms and the nearest tantalum atoms, respectively. The feature at approximately 3 Å in the transform for the KOH treated film, probably corresponds to scattering from potassium, but its greater width suggests that there is disorder in the tantalate layer. The absence of scattering from the nearest Ta atoms for the KOH treated film demonstrates the decreased long range order for the $KTaO_3$ in the film with respect to the standard powder as suggested by the inhomogeneous broadening seen in the XANES spectrum. Both transforms are clearly different than that seen for Ta_2O_5 and TaN and agree with EXAFS results reported previously for $KTaO_3$ [11]. Thus, the x-ray absorption spectra are consistent with the presence of $KTaO_3$ on the surface of sputtered TaN films exposed to KOH.

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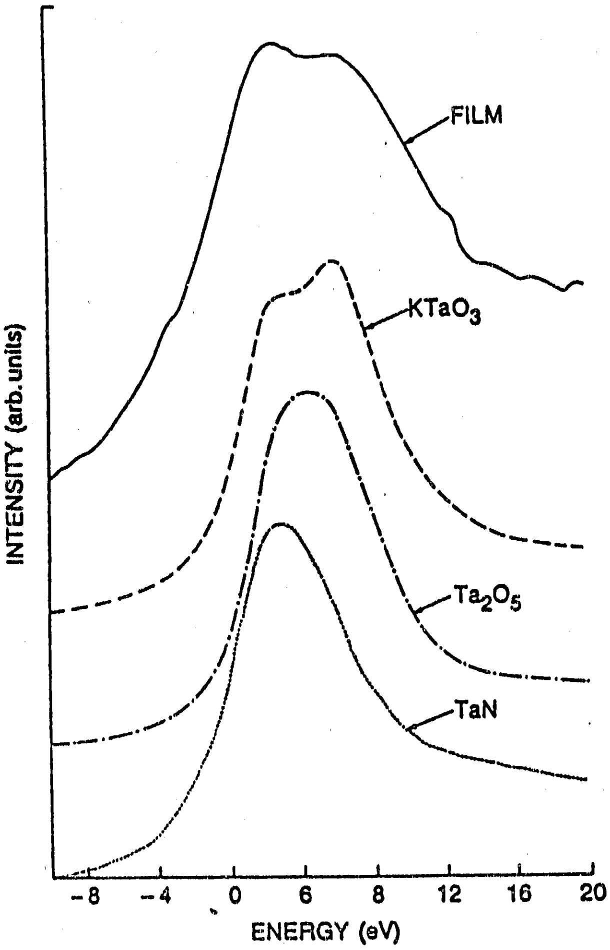

Figure 1--X-ray absorption relative to the Ta L_{III} edge at 9881.1 eV for a TaN film exposed to KOH and standard $KTaO_3$, Ta_2O_5, and TaN powders.

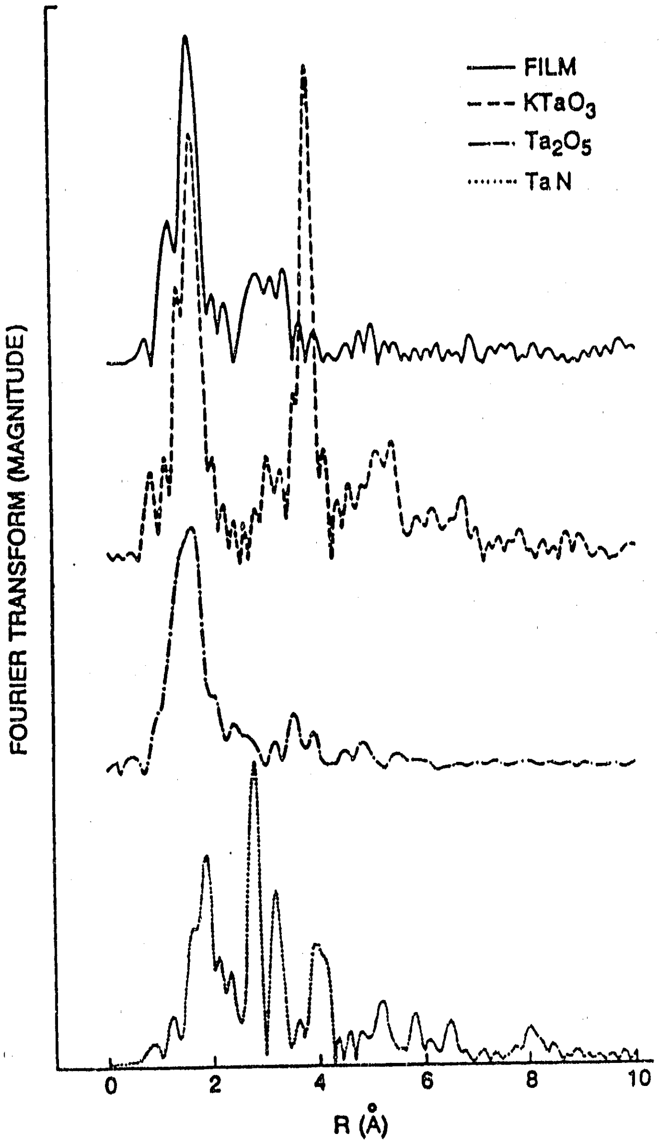

Figure 2--Fourier transforms of EXAFS spectra of a TaN film exposed to KOH and standard $TaKO_3$, Ta_2O_5, and TaN powders relative to Ta L_{III} (E_0 = 9881.1eV).

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