

New Niobium Pentoxide (Nb_2O_5) Integrated Capacitors for Decoupling Applications

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Abstract

Integrated capacitors are attractive to the electronics industry as they potentially consume less space and show lower parasitics compared with their surface mount counterparts. One of the major applications is their use as decoupling capacitors in printed circuit boards or chip package substrates. Tantalum oxide (Ta_2O_5) has been shown to be an excellent candidate for integrated decoupling because of its relatively high dielectric constant ($k \sim 24$) and the ability to form sub-micron thick layers. Increasing circuit density calls for even larger capacitance density than can be provided by Ta_2O_5 . To obtain higher density, stacking of planar capacitors has been done by various researchers. This can provide high capacitance per unit area, but involves too many process steps, making the technique not very cost effective. Thus, there is the need for a dielectric material with a higher dielectric constant that can deliver high capacitance density with a simple planar geometry.

Niobium pentoxide (Nb_2O_5) with a $k \sim 41$ is a promising material for planar applications. Nb_2O_5 is a proven dielectric material for electrolytic type surface mount capacitors. Also, lower cost and better availability are driving niobium oxide as an alternative to the tantalum oxide dielectric. In this paper, we report niobium oxide used to fabricate thin film capacitors that can give a significantly higher capacitance density than the tantalum oxide dielectric. However, oxygen has a higher solubility in niobium than in tantalum, which can lead to the formation of sub-oxides along with the desired Nb_2O_5 . These suboxides are partly conducting and can create paths for high leakage currents. Niobium oxide has been formed by reactive sputtering, and by anodization. We present details of the material characterization using both of these methods. Another issue addressed is the oxygen diffusion from the dielectric to adjacent layers. This can occur when the dielectric is exposed to high temperatures. The potential for a diffusion barrier of niobium nitride (NbN) deposited above and below the dielectric forming a 'sandwich' structure is indicated by results using TaN with tantalum capacitors.

Keywords: Anodization, Reactive Sputtering, Niobium Oxide

Introduction

The increasing density of ICs in electronic systems, the speed of operation, and the resulting power density, place larger demands on PWB power distribution systems and thus on discrete or integrated decoupling capacitors. The University of Arkansas has a long history of work in integrated decoupling capacitors based on thin film Ta_2O_5 dielectric, providing 100 nF/cm² capacitance density for 2000Å dielectric, up to 600 nF/cm² for a triple layer 1000 Å thick dielectric. [1, 2] However, niobium pentoxide, with a higher dielectric constant, $k \sim 41$, can give higher capacitance per unit area compared with tantalum. Niobium capacitors have already established their market in the area of electrolytic surface mount capacitors. This paper describes our effort to extend Nb_2O_5 capacitors into thin film technology. Niobium oxide may be deposited using a number of techniques, including reactive sputtering, sol-gel, chemical spray pyrolysis, CVD, ALD, anodization, etc [3 - 10]. In this paper, we have used

reactive sputtering and anodization to form Nb_2O_5 dielectric layers and capacitors.

We present the material characterization of the reactively sputtered niobium oxide and anodically oxidized niobium oxide, in order to examine the stoichiometry. We also look at early results of capacitor fabrication.

Experimental Procedure

Anodized Niobium Oxide Characterization:

Oxidized five-inch diameter p-type Si (111) wafers were used as substrates. The wafer was back sputtered for 60-seconds and a niobium film of 5500Å was deposited by DC magnetron sputtering at 2200 W and an argon pressure of 5 mTorr. Anodization details are given in the Capacitor Fabrication section.

Reactively Sputtered Niobium Oxide Characterization:

Oxidized silicon [p-Si (111)] substrates were back sputtered for sixty seconds as above. Niobium

oxide was deposited at 500 W using a mixture of Ar/10%O₂ at a pressure of 10 mTorr. The wafer was allowed to cool for five minutes in the chamber before taking it out of the system.

Capacitor Fabrication:

The test vehicle for capacitors consists of copper top and bottom plates with niobium oxide dielectric in between. A Varian XM-8 DC magnetron sputtering system was used for sputtering top and bottom plates as well as niobium metal or reactively sputtered niobium pentoxide. This system has individual chambers for each metal target which helps to avoid cross-contamination. The sputtering chamber was maintained at 10⁻⁶ Torr by a cryogenic pump. Fabrication steps for these capacitors are given below:

Similar substrates used for anodized films and reactively sputtered films were used for device fabrication. Initially, the wafer was thermally oxidized to obtain a 2-micron thick SiO₂ on both sides of the wafer to provide insulation between the substrate and the subsequent device layers. Thickness of the oxide was measured by using a Nanospec reflectometer. After thermal oxidation, prior to metal deposition, the wafer was back sputtered for 60 seconds to roughen the wafer surface in order to improve the metal adhesion. Then a titanium layer of 500Å thick was deposited as an adhesion layer for copper. Copper of 2 µm thickness was deposited as the bottom plate. For anodized capacitors, this was followed by a 1500Å niobium film. Anodization was carried out at room temperature (20°C) in a tartaric acid-ethylene glycol-DI water solution. The anodization bath contained a 1:3 mixture of 5.3% tartaric acid aqueous solution and ethylene glycol. The solution had a pH of 2.2 at room temperature. Niobium pentoxide (Nb₂O₅) was formed by a sequence of constant current and constant voltage. Initial current was calculated based on a current density of 0.5 mA/cm². For a 125-mm diameter wafer, the initial current was 61 mA and the final voltage was set to 83 V. This anodization voltage was calculated assuming 24 Å/V formation relationship described in the literature [11, 12]. Total time was about 40 minutes for a final current of 1 mA, of which the constant current regime lasted for the initial 8 minutes. A pale green color dielectric was obtained at the end of the anodization.

Following anodization, a top copper layer of 2 µm thickness was sputtered on the dielectric. One millimeter square top plates were patterned with a 2.5 µm AZ4110 resist and copper etching was performed. Photoresist was then stripped off the wafer using acetone and resist strip, AZ300T at 90°C. The common bottom plate contact was formed by

removing a small area of dielectric at the wafer edge and sputtering 1 µm of copper onto a shadow-masked area, completing the test vehicle fabrication. The final capacitor structure is shown in Figure 1.

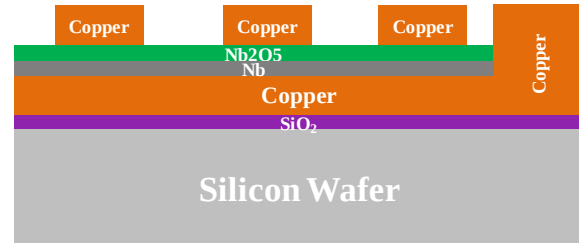


Figure 1: Schematic of Nb₂O₅ test capacitors with anodized dielectric.

Reactively sputtered capacitors were also formed the same way as described above, except that the anodization step was replaced by reactive sputtering as previously described. Thus, the final metal stack contains Copper-Nb₂O₅-Copper plates.

Results & Discussion

Dielectric film characterization was carried out first, in order to ensure that the desired Nb₂O₅ was formed by both anodization and reactive sputtering. The chemical composition of the anodized film was studied using a Kratos Axis 165 Photoelectron Spectrometer with a Mg K_α X-ray source. Films were analyzed in the as-deposited state and after sputter cleaning of the surface for 60 seconds. This sputter cleaning was done to ensure a contaminant-free surface for composition analysis. Argon ions were used for sputtering and approximately 100 Å of the surface was etched. The sputter rate was determined with a Ta₂O₅ sample under identical sputtering conditions. XPS spectra were handled using XKRATOS software. Initially, the binding energy scale was calibrated by setting the carbon peak, C 1s at 284.6 eV as the reference. Deconvolution of the spectra and linear background subtraction was done to obtain binding energies of each element and the amount of different compounds present in the film. Each binding energy peak was matched with the Nb₂O₅ reference XPS data available in the National Institute of Standards and Technology (NIST) X-ray Photoelectron Spectroscopy Database to identify the valence of each element [13]. After obtaining the matching binding energy peaks, the areas under the peaks were calculated to give the amount of each compound in the film. XPS data obtained for the anodized film and the reactively sputtered film are discussed below.

A. Anodized Dielectric

Initial Surface Analysis:-

Figure 2 shows the XPS spectra of an original anodized niobium oxide dielectric, taken from the center of the wafer. Figure 2 (a) shows the typical doublet found in the Nb 3d spectrum. The binding energy (BE) of the major peak matches the BE of Nb 3d_{5/2} spectral line, 207.2 eV with an accuracy of ± 0.2 eV indicating the presence of Nb₂O₅. This peak area amounts to 60% of the total area. For the second peak located at 209.7 eV, the closest match found was at 210.2 eV of Nb 3d_{3/2} spectral line. Since these spectral lines are 0.5 eV apart, the minor peak could be an indication of the presence of a non-stoichiometric oxide in the film. Another possibility is the presence of hydrogen niobium oxides, whose peak BE is at 209.9 eV for Nb 3d_{5/2}, only 0.2 eV apart from the observed peak BE. Therefore, from the peak BE analysis, the as-deposited anodized film contains at least 60% of the desired Nb₂O₅.

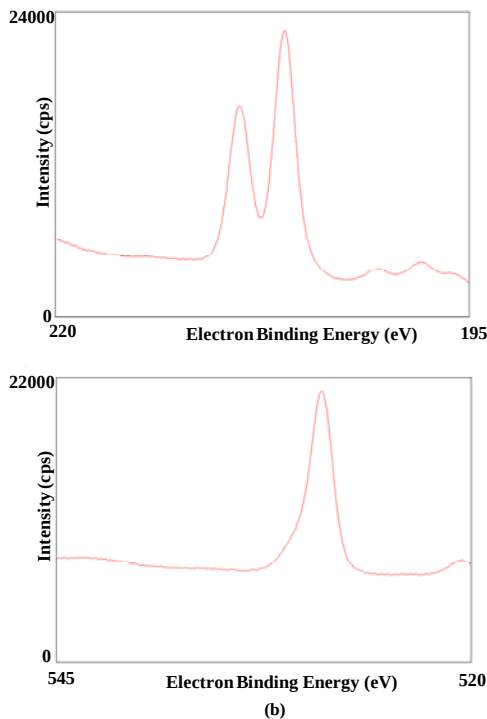


Figure 2: XPS spectra of the CENTER niobium oxide thin film anodized at 83 V and 0.5 mA/cm² current density: as deposited (a) Nb 3d and (b) O 1s.

The oxygen spectra major peak in Figure 2 (b) matched the BE of O 1s spectral line, 529.6 eV with an accuracy of ± 0.2 eV, contributing to Nb₂O₅. Also, deconvolution exposed a second peak which can be seen as a widening of the left hand side,

towards the baseline of the peak. The BE of this minor peak matched the spectral line (O 1s), 531.3 eV for Nb₂O₅, but there is a possible suboxide peak between these two. Thus, the oxygen spectrum of the anodized oxide gives a very high Nb₂O₅ presence in the film.

Analysis after Ar⁺ etching:-

In order to remove the surface contaminants, the film was sputter etched with the Ar beam, removing about 100 Å of the film surface. Figure 3 shows the Nb 3d and O 1s spectra taken after etching. Deconvolution and peak BE matching of the niobium spectra indicate the presence of about 74% Nb₂O₅, 19% NbO and Nb mixture, and the rest NbO_x/Nb. The major peak of oxygen spectrum matches the BE of O 1s spectral line, indicating Nb₂O₅.

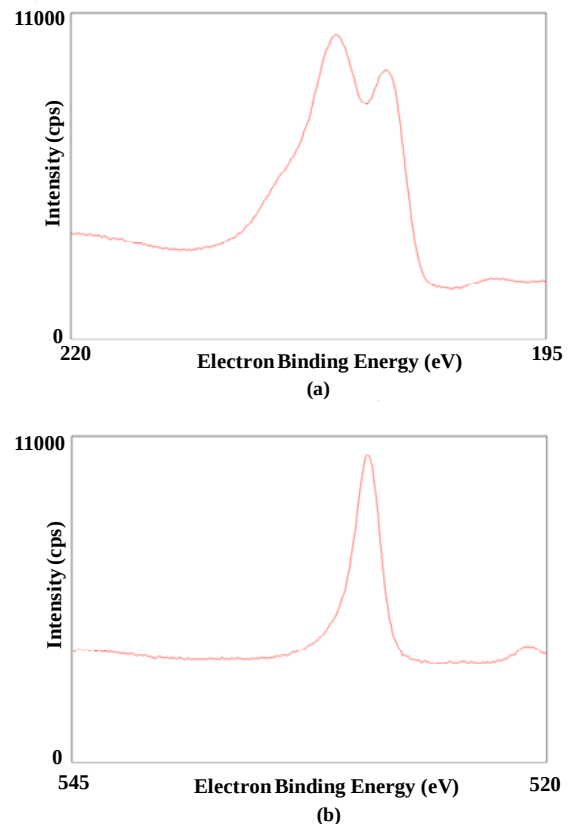


Figure 3: XPS spectra of the CENTER niobium oxide thin film anodized at 83 V and 0.5 mA/cm² current density: after Ar etching (a) Nb 3d and (b) O 1s.

B. Reactively Sputtered Dielectric

Initial Surface Analysis:-

Figure 4 shows the Nb 3d and O 1s spectra of the reactively sputtered niobium oxide. Similar to the anodized film spectra, one doublet can be seen for the Nb 3d spectrum. In this case, both major and

minor peaks' binding energies show 100% presence of Nb_2O_5 . The major peak matches exactly with the binding energy of 207.2 eV for Nb 3d_{5/2} and the minor peak at 210.2 eV $\pm$ 0.2 eV for Nb 3d_{3/2} spectral line. Also, we can look at the doublet separation and match with that on the database to decide, if the compound obtained is the desired one. For Nb_2O_5 , Nb 3d doublet separation should be 2.5 eV or 2.8 eV. In this case, doublet separation exactly matches to 2.8 eV for Nb_2O_5 . For oxygen spectra, even though deconvolution gives two peaks, only the major peak is considered for analysis, as the maximum contribution, 83% comes from that peak. The major peak BE matched with 530.1 $\pm$ 0.1 eV for Nb_2O_5 . In essence, surface analysis of the reactively sputtered oxide film gives the desired dielectric composition.

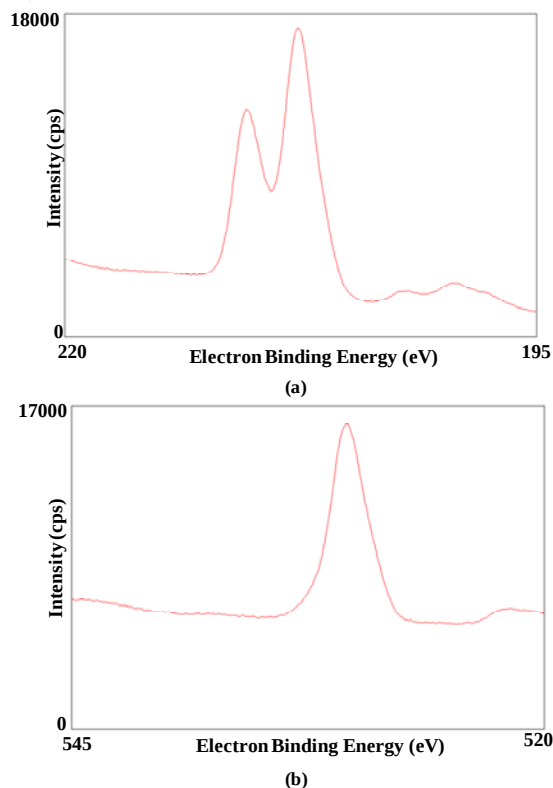


Figure 4: XPS spectra of the REACTIVELY SPUTTERED niobium oxide thin film in the as-deposited state: (a) Nb 3d and (b) O 1s.

Analysis after Ar^+ etching:-

Spectra taken after Ar^+ etching are shown in Figure 5. Similar to the data from the initial surface spectrum, the major peak in Nb spectrum matched the BE of Nb 3d_{5/2} 207.1 eV $\pm$ 0.1 eV. But, the closest match for the minor peak was NbO. The third peak from the deconvolution, which amounts to

about 5% of the total area, indicated the presence of a mixture of Nb and NbO_x . This reduction in oxygen and peak shift may be explained as a result of chemical alterations that can take place during Ar etching. It is also possible that the etching causes localized heating which can increase oxygen mobility in the film, leading to oxygen diffusion out of the oxide.

The BE analysis of the oxygen spectrum showed a 100% Nb_2O_5 in the film. Thus, we can say that the reactively sputtered film at 500 W and 10 mTorr Ar/O_2 pressure will give us the desired Nb_2O_5 .

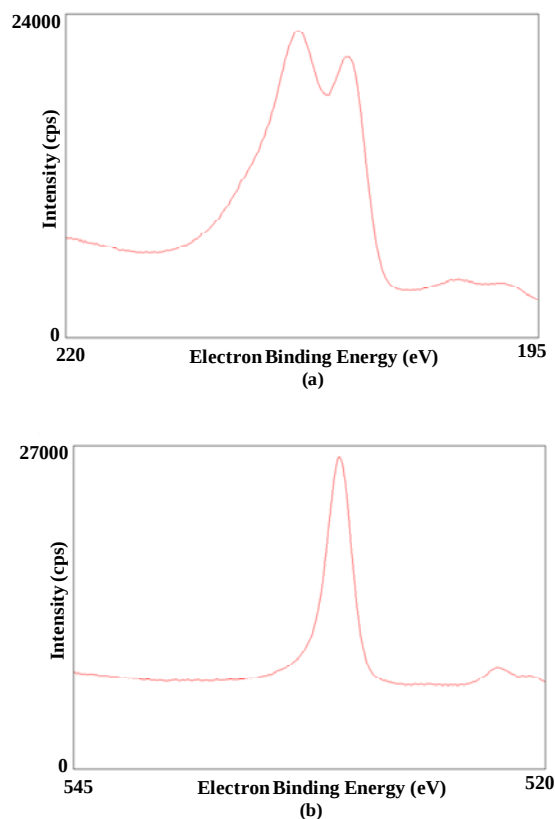


Figure 5: XPS spectra of the REACTIVELY SPUTTERED niobium oxide thin film after Ar^+ etching: (a) Nb 3d and (b) O 1s.

All the results discussed above based on niobium spectra are summarized in Table 1.

From the table, we can see that the Nb_2O_5 percentage in the anodized film increased after Ar etching whereas in the reactively sputtered film, the percentage of Nb_2O_5 decreased after etching. This may be explained as follows. Auger depth profile analysis of the anodized sample showed a low oxygen concentration area near the surface and an increased oxygen concentration as the sample was

sputtered deeper. From the Auger data, oxygen concentration increased from 50 at.% on the surface to 56 at.% at 100 Å into the surface. Since the Ar etching removes about 100 Å film from the surface, the higher oxygen concentration region is exposed, indicating a greater concentration of Nb₂O₅. This coupled with the localized heating may give rise to a mixture of low valence niobium oxide compounds.

		Nb ₂ O ₅	NbO/ Nb	NbO _x / Nb
Anodized	Initial Surface	60%	—	—
	After Ar⁺ Etching	74%	19%	7%
Reactively Sputtered	Initial Surface	100%	—	—
	After Ar⁺ Etching	77%	—	5%

Table 1: Percentage of Nb-O compounds present in the anodized and reactively sputtered dielectric before and after Ar⁺ etching.

In order to check the anodization uniformity across the wafer, a sample was taken from the left side of the wafer along the line of the CENTER sample. Like other samples, both the initial surface and sputter cleaned surface of the LEFT sample were analyzed.

Initial Surface Analysis:-

Figure 6a and 6b shows the niobium and oxygen XPS spectra of the LEFT sample before Ar⁺ etching. The major peak exactly matches with the BE of Nb 3d_{5/2} spectral line, 206.9 eV. This amounts to about 64%. Similar to the CENTER sample, the second peak, at 209.6 eV is no match to Nb-O compounds; except for the hydrogen niobium oxide whose BE is at 209.9 eV. Thus, the initial surface results obtained for the LEFT and the CENTER samples are very much the same as expected and they show only a 4% difference in the amount of Nb₂O₅. Deconvolution of the oxygen spectra gave two peaks, out of which the major peak matched the BE of O 1s spectral line, 531.3 eV for Nb₂O₅. Thus, for oxygen spectra, 83% of the photoelectrons came from niobium pentoxide.

Analysis after Ar⁺ etching:-

The niobium and oxygen XPS spectra of the LEFT sample after Ar etching are shown in Figure 7a and 7b. Deconvolution of the spectra gave three peaks and the third hidden peak is on the left side of the peaks close to the baseline. Major peak BE, 207 eV corresponds to the spectral line Nb 3d_{5/2} and the

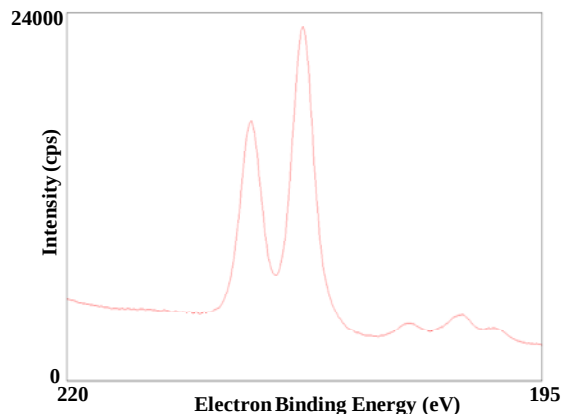


Figure 6a: XPS spectra (Nb 3d) of the LEFT niobium oxide thin film anodized at 83 V and 0.5 mA/cm² current density: as-deposited.

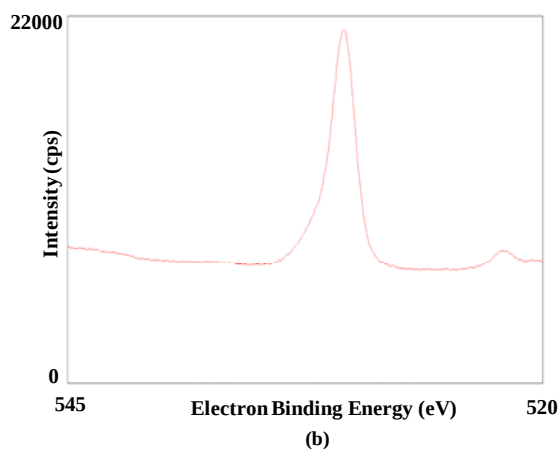


Figure 6b: XPS spectra (O 1s) of the LEFT niobium oxide thin film anodized at 83 V and 0.5 mA/cm² current density: as-deposited.

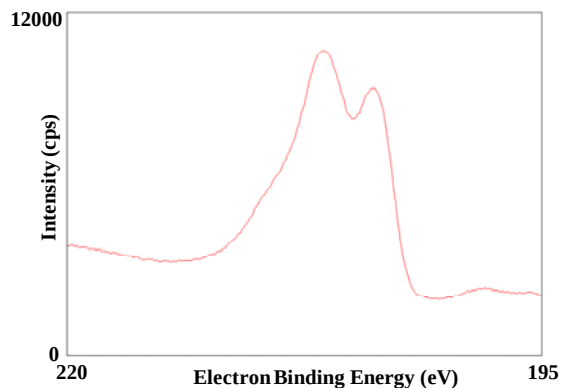


Figure 7a: XPS spectra (Nb 3d) of the LEFT niobium oxide thin film anodized at 83 V and 0.5 mA/cm² current density: after Ar⁺ etching.

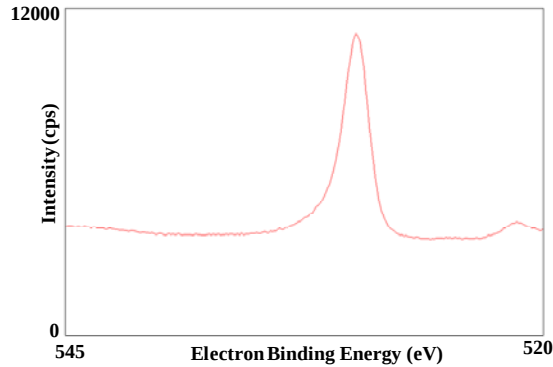


Figure 7b: XPS spectra (O 1s) of the LEFT niobium oxide thin film anodized at 83 V and 0.5 mA/cm² current density: after Ar⁺ etching.

minor peaks amounting to 17% and 7% of the total area, had peaks at 204.1 and 210.7 eV. All had an accuracy of ± 0.2 eV, except for the peak with 17% area that is 0.3 eV from the Nb 3d_{5/2} spectral line. So, the results obtained for the LEFT sample are not much different from those obtained for the CENTER sample. The major peak BE, 530.3 eV obtained for the oxygen spectra exactly matches with that of Nb₂O₅.

The data obtained for the anodized CENTER sample and the LEFT sample from their XPS spectra are summarized in Table 2.

		Nb ₂ O ₅	NbO/ Nb	NbO _x / Nb
CENTER	Immediate Surface	60%	—	—
	After Ar ⁺ Etching	74%	19%	7%
LEFT	Immediate Surface	64%	—	—
	After Ar ⁺ Etching	77%	17%	6%

Table 2: Nb-O compounds present in the CENTER sample vs. LEFT sample.

From the table, we can see that there is a slight difference in the amount of niobium oxide present in the center of the wafer compared with the left edge of the wafer. This difference, about 3-4%, could be a result of slightly higher current density close to the edges with respect to the wafer center. Increased current densities give rise to improved mobility of the ions; especially the oxygen ions become more mobile since they are lighter compared with the niobium ions, which can result in a more saturated oxide. The increase in Nb₂O₅ content after

etching and the presence of NbO-Nb mixtures are explained earlier in the paper.

So, a reactively sputtered film gives 100% Nb₂O₅ film on the surface whereas, the oxide film anodized in ethylene glycol-water-tartaric acid solution gives only 60% Nb₂O₅ on the surface. Since Auger spectroscopy showed the increasing oxygen content trend inward the oxide, it can be assumed that the film thickness, closer to the niobium metal will contain higher order oxides, like Nb₂O₅. Further analysis such as sputter profiling will be done on the anodized film to determine the film composition all the way through the oxide.

Niobium Oxide Capacitors

Capacitors were fabricated with both anodized and reactively sputtered dielectrics. Reactively sputtered films of 2000 Å and 1050 Å thickness and anodized films of 2500 Å thickness were used. Fabricated capacitors were tested for capacitance to calculate the dielectric constant. The test vehicle design consisted of an array of 4410 capacitors of 1 mm × 1 mm size.

The capacitors formed with reactively sputtered niobium oxide of 2000 Å thickness gave an average capacitance value of 1.9 nF, giving a $k \sim 43$. This ' k ' value agrees with the value reported in the literature ($k \sim 41$) [10]. Measured capacitances for this 2000 Å thick dielectric ranged from 1.87 nF to 1.99 nF. Yield could not be obtained from the wafer due to measurement problems with the two-probe tester for high capacitance values around the center of the wafer.

Capacitors were also fabricated with a reactively sputtered thinner dielectric, 1050 Å, and the measured capacitances averaged to be 3.4 nF, giving a dielectric constant of $k \sim 40$. Measured capacitances ranged from 3.2 nF to 3.6 nF. This variation in capacitance can be related to the sputter thickness non-uniformity across the wafer.

The capacitors formed with the anodized dielectric also showed high capacitance measurements in the center of the wafer. This could be caused by wafer overheating during top plate sputtering. Overheating can cause oxygen to diffuse from the dielectric, leading to a reduction in the effective thickness of the dielectric. In order to solve this problem, further investigations will be carried out using evaporated top plates, instead of sputtered plates. Another issue found with this anodized dielectric was that the measured capacitances gave values much higher than anticipated. For example, for the 2500 Å thick dielectric, the measured capacitance averaged 2.6 nF, which would indicate that the effective dielectric thickness is less than calculated. This may result from a number of

mechanisms. First of all, if the anodized film formed is not a single layer of Nb_2O_5 , but composed of multiple layers of Nb-O compounds of varying oxygen concentrations, the effective thickness of the desired Nb_2O_5 will be reduced, giving a high capacitance. This will be investigated by sputter profiling the oxide film and using transmission electron microscopy (TEM) for electron diffraction to separate phases, if any.

Another reason could be the heating of the anodized film during top copper sputtering. That heating may be sufficient to create oxygen diffusion in the dielectric, lowering the effective thickness of the Nb_2O_5 dielectric. In this case, sputter heating affects the entire anodized film and is worse in the center, unlike the reactively sputtered dielectric which is seen to be primarily affected in the center. The reason could be the already oxygen deficient (60-64% Nb_2O_5) anodized surface being heated up. It was also noticed that, even though the original anodized film showed unmeasurably high surface resistance, it gave megohm-range values after processing. Cross-sectional analysis of the anodized film will be done to investigate if the anodized film is dense or porous, which will affect the properties of the film. These issues will be analyzed and results will be presented at the conference.

Conclusions

Reactive sputtering gives a complete Nb_2O_5 dielectric, whereas the anodized film in ethylene glycol-water-tartaric acid solution gives only 60-64% Nb_2O_5 on the surface. Changing the anodizing solution is an option to investigate for effects on the stoichiometry of the film. The anodized film shows a slight stoichiometric variation across the wafer as seen from the samples taken from the center and the left of the wafer. Capacitors fabricated with 2000 Å Nb_2O_5 dielectric confirmed the $k \sim 43$. Results obtained from fabricated capacitors are encouraging, but still more work needs to be done to optimize all the parameters to realize high yield planar high- k Nb_2O_5 embedded capacitors.

Acknowledgements

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