Characterization and electrical response of reactively sputtered thin film deposited at oxygen and nitrous oxide environment

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Abstract

Niobium oxynitride (NbON) thin films were deposited on silicon substrate using DC reactive magnetron sputtering technique of niobium metal targets at different nitrous oxide (N_2O) and oxygen flow in the plasma during deposition. To get NbON thin films, the deposition parameters were also optimized. X-ray reflectivity (XRR) technique was used to estimate the film thickness of the as deposited films. The films' surface morphology and chemical compositions were investigated by field-emission scanning electron microscopy (FE-SEM) and x-ray photoelectron spectroscopy (XPS) techniques. SEM images indicate the smooth surface morphology of the deposited films. XPS study exposes the noticeable presence of N_2 in the niobium oxynitride films deposited with only 20 sccm nitrous oxide flows in the plasma. The leakage current-voltage (*I*-*V*) measurement reveals the reduction in leakage current with higher N_2O and lowers oxygen flow rates. The resistivity of the thin films was measured. The thin films deposited with higher N_2O flow give high resistivity because of lesser availability of defect states. It may be stated that nitrous oxide content reduces the leakage current thus, improves the film and interface properties.

Keywords: *DC reactive magnetron sputtering, Oxynitride thin-films, X-ray photoelectron spectroscopy, Leakage current, Oxygen vacancy*

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1. Introduction

In recent times oxynitride thin-films are studied widely due to their extensive applications in electronic and optoelectronic devices with novel physical properties [1, 2]. Oxynitride films of a single metal and bimetal are also investigated as a catalyst [3]. Lithium phosphorus oxynitride has been used as a solid electrolyte in thin film battery applications. Zinc oxynitride is a vital substitute for a conventional semiconductor film such as silicon due to its high mobility value [4, 5]. Reactive sputtering is the very familiar technique used to develop these Oxynitride thin films [6]. Film properties like structural and physical properties directly depend on the deposition parameters. In this work, niobium oxynitride

(NbON) thin films have been fabricated using DC reactive sputtering technique by introducing N_2O and oxygen into the argon (Ar) plasma during the deposition. The surface characterization and electrical properties of the as deposited thin films have been explored to allow N_2O in the deposition chamber.

2. Experimental

NbON thin films were deposited using DC reactive sputtering process. Si (100) wafers with the resistivity of 0.1– 0.5 Ω-cm of area 1cm×1 cm were used as substrates. Then the substrates were cleaned by standard RCA-I and RCA-II cleaning methods to eradicate possible contaminants [7]. After that, the substrates were rinsed into 1% HF solution for 60 seconds and immediately taken into the sputtering chamber. A metallic niobium target (purity 99.8%) was sputtered in a $Ar/O_2/N_2O$ atmosphere in DC mode. During deposition, the oxygen and N_2O flow rates were varied, keeping the argon flow rate fixed at 35 sccm. Sample names and different gas flows are tabulated in Table 1. XRR measurements were performed using a Rigaku SmartLab 3 kW, X-ray diffractometer. The XPS system (VSW Ltd. UK) technique has been employed to identify elements present in the films. The measurements were carried out using non-monochromatic Mg K_α (Energy = 1253.6 eV) x-ray source and ejected photoelectrons collected by a hemispherical electron analyzer with a 150 mm mean radius. To analyze the XPS data CasaXPS software has been used. The C 1s peak (284.8 eV) was used as the reference for survey scan calibration to compensate for any charge-induced shift [8]. The background signals of XPS curves were subtracted by the Shirley method. The XPS spectra were deconvoluted using the Gaussian–Lorentzian function to identify various peaks in the spectra. The surface morphology of the films was analyzed using (FE-SEM) technique. A 300 nm thick titanium layer was then evaporated on the oxynitride film by electron beam evaporation system. Then 100μm diameter top electrodes were patterned using the UV photolithography technique. For electrical characterization, Ti/NbON/Si-based metal-oxide-semiconductor (MOS) device has been fabricated. The *I–V* and resistivity behavior of all the devices were studied using a 4200-SCS semiconductor parameter analyzer equipped with PA-4200 pre-amplifiers.

Table 1. Nomenclature of all the reactively sputter deposited thin-films.

Sample name	Argon flow (sccm)	Oxygen flow (sccm)	Nitrous oxide flow (sccm)
N5	35	15	5
N10	35	10	10
N15	35	5	15
N20	35	0	20

3. Results and discussion

A schematic diagram of Ti/NbON/Si based MOS devices is shown in FIG 1.

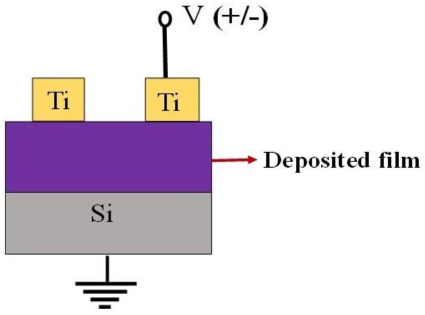

FIG 1. Schematic diagram of the MOS capacitor structure with measuring circuit used in this study.

3.1 Thickness measurment

FIG. 2 shows the x-ray reflectivity profile of all the samples. It has been found out that the film-thickness increases with increasing N_2O content in the plasma. Thickness of N5, N10, N15 and N20 are 18.02, 19.06, 19.28 and 28.41nm, respectively.

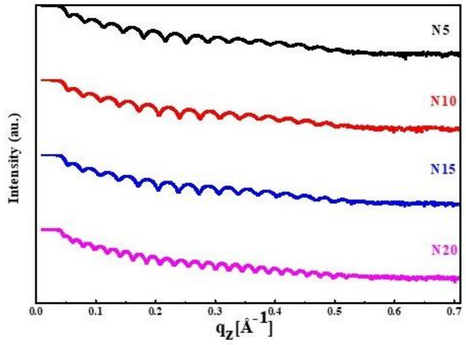

FIG 2. X-ray reflectivity (XRR) graph of four different samples.

3.2 Chemical composition

To investigate the chemical compositions of the oxynitride films XPS technique was introduced. The XPS survey scans ranging from 0 to 800 eV binding energy are shown in FIG 3(a). The peak observed at 284.8 eV is corresponding to C 1s and can be ascribed as adventitious carbon. In the full survey scan of N5, N10, and N15 samples, no significant peak for nitrogen has been observed, indicating that flow rates of oxygen and N_2O are insufficient to allow nitrogen doping. But in N20, some peaks were observed at a binding energy of 399±0.2 and 401.7±0.2 eV, attributed to adsorbed nitrogen [9]. Nitrogen peaks arise at low binding energy in the oxynitride film owing to **N=0** bonds. As the nitrous oxide flow increases in the plasma during deposition, the amount of oxygen in the film decreased. So, when sufficient N_2O gas is allowed in the chamber, oxygen ions are partially substituted by nitrogen ions in the film's structure. XPS results provide that for the highest N_2O flow in the chamber, the active N species readily competed for sites and substituted oxygen in the films. High resolution spectra of Nb 3d, O1s, N1s and C 1s are analyzed for Nb20 sample shown in FIG 3(b). The O1s high resolution spectra of N20 has two peaks at 530±0.3 eV and 531.1±0.3 eV represent lattice oxygen and oxygen vacancy, respectively [10].

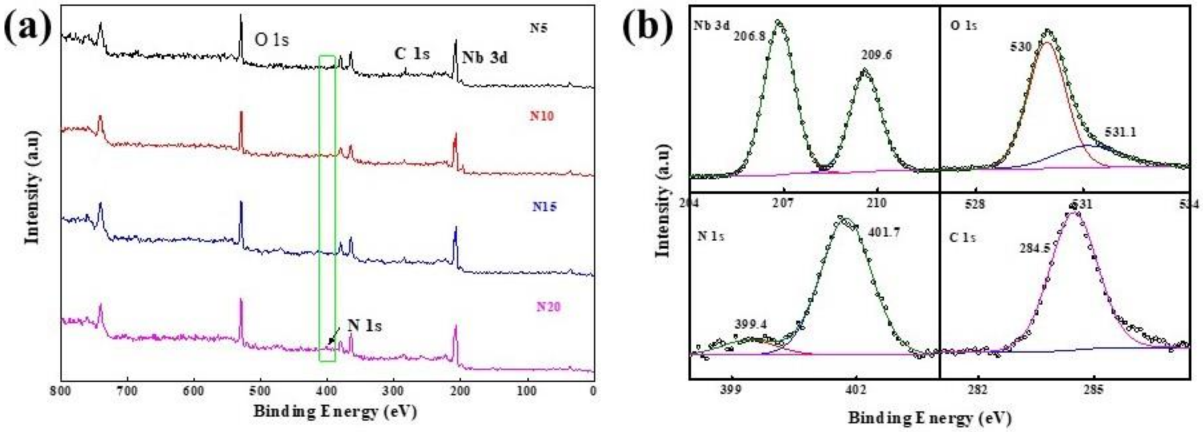

FIG 3. (a) XPS survey analysis for all the samples. (b) High resolution spectra of Nb 3d, O1s, N1s and C 1s for N20 sample. Scattered points represent experimental data.

3.3 Surface morphology

SEM micrograph of N20 sample is shown in FIG 4. The current work provides fabricated niobium oxynitride in a highly ordered and uniform structure.

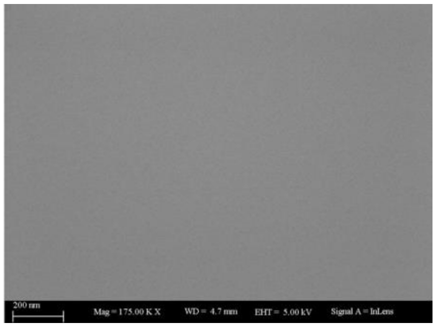

FIG 4. SEM image of N20 thin film deposited at O_2/N_2O gas flow ratio 0:20. The scale bar represents 200 nm.

3.4 Electrical characteristics

The resistivity (ρ) of the thin films has been measured and shown in FIG 5. The figure confirms that the resistivity of the film increases with higher N_2O in the plasma during deposition. It may be explained on the basis of oxygen vacancies created during the production of the film. Oxygen vacancies can be predicted as free charge carriers, which may be formed during the film's production or during gate voltage biasing. Oxygen vacancy acts like a donor. When nitrous oxide is allowed to the chamber during deposition, oxygen is replaced by the nitrogen generating new phases. So, the amount of oxygen vacancy gets reduced. As a result carrier concentration in the film reduces. When carrier concentration decreased as the nitrogen in the films increased, the resistivity increased.

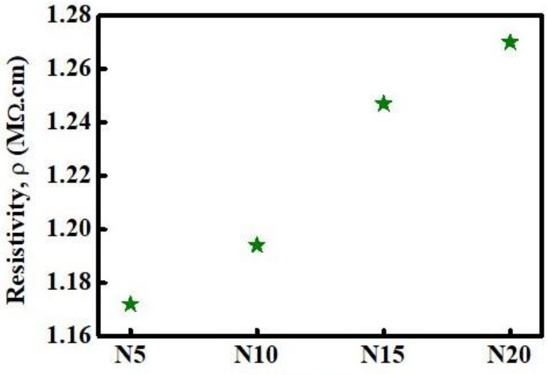

FIG 5. Dependence of electrical resistivity on various O_2/N_2O gas flow in magnetron chamber.

FIG 6(a) shows the leakage current (I) vs. gate voltage (V) characteristic of the MOS structures. The reduction in leakage current with higher N_2O and lower oxygen flow rates is observed. The lowest leakage current of the order of 10^{-6}–10^{-5} A was observed for the devices of the N20 sample. The leakage current of the films deposited with 0-15 sccm N_2O flow is high due to oxygen vacancies. However, the leakage current was considerably reduced for the films grown with high N_2O flow probably due to the smaller number of oxygen vacancies. [11]. Reduction of leakage current attributes to the improvement in NbON/Si interface and deposited film properties. The leakage current (I) vs. applied bias voltage (V) curves measured for N5, N10, N15 are more or less the same, but for N20, it shows a slightly different nature in the higher field zone. This is because of the variation of oxygen vacancy with N_2O concentration. To understand the current transport mechanism of the Ti\NbON\Si MOS structure, the (*I* - *V*) curves in the positive region for all the devices have been plotted in the double logarithmic scale and displayed in FIG 6(b). The plots are nearly straight line at the low field region for all the devices. The current transport mechanism varied with the applied bias field. Small numbers of free electrons coming off from defect states are drifted according to Ohm's law at low fields. High gate voltage application on the device induces large charge injection from the substrate to film and vice versa, which increases leakage current density. The non-ohmic current-voltage relation observed at high voltage region is fitted linearly with $\ln I \sim V^{1/2}$ and shown in the inset of FIG 6(b). The transport mechanism of defects in this voltage region in the film indicates a Schottky emission conductive mechanism [10].

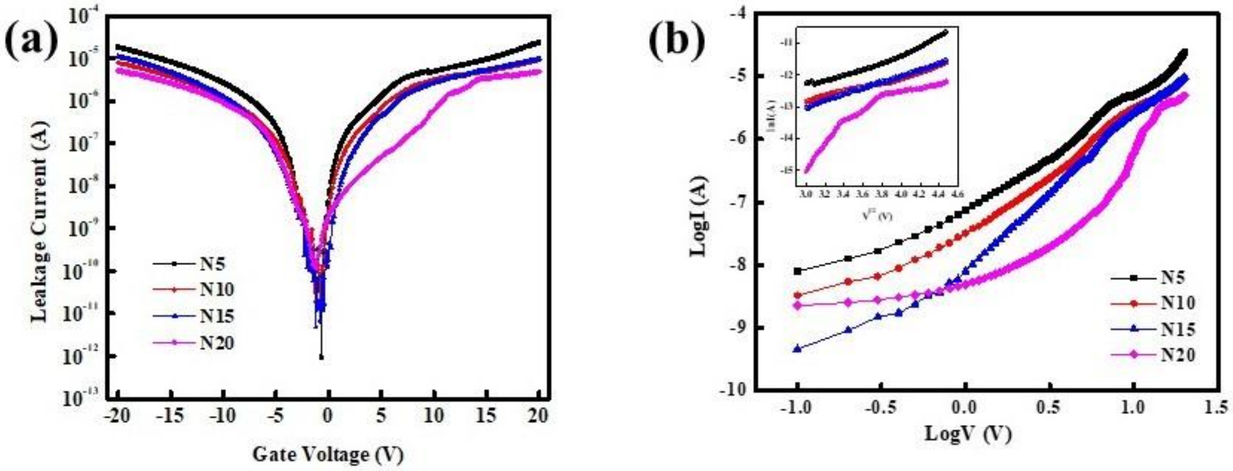

FIG 6. (a) Relation between leakage current and gate voltage for all the samples measured at room temperature. (b) Double logarithmic $I-V$ plot for N5, N10, N15 and N20. The inset shows the fitting of the $I-V$ curve with lnI ~ $V^{1/2}$ plot.

4. Conclusion

The structural composition and electrical properties of the as deposited films were studied as a function of the N_2O flow provided in the plasma during deposition. After analysing XPS data, one can easily conclude that the sample prepared with 20 sccm N_2O flow produced Niobium oxynitride film. The nitrous oxide flow affects the structural properties of the film. So, a slight change has been observed in the electrical properties of the films with an increase in nitrous oxide flow rate. When oxygen vacancy decreased as the nitrogen in the films increased, the resistivity increased. The sample grown with 20 sccm nitrous oxide flow exhibited the lowest leakage current. The leakage current variation with gate voltage followed Ohm's law and the Schottky emission conductive mechanism at low and high fields, respectively. The above discussions show that when 20 sccm N_2O is introduced into the chamber, Niobium oxynitride forms. Due to significant reduction of leakage current deposited film properties improved.

5. Acknowledgements

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