RF Magnetron Sputtering Process of P-Type NiO Thin Films Suitable for Mass Production of Compound Semiconductor Devices

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Non-stoichiometric nickel oxide (NiO) thin films can exhibit p-type semiconducting properties and possess wide band gap (3.6-4.0 eV) and simultaneously low electrical resistance, when film growth conditions lead to generating nickel vacancies and/or forming interstitial oxygen atoms in NiO crystallites [1, 2]. It was shown that resistivity of the films deposited by radio-frequency (RF) reactive magnetron sputtering in Ar-O_2 gas mix decreased as oxygen partial pressure increased. Films with the lowest resistivity can be obtained when sputtered from NiO target in pure oxygen atmosphere on unheated substrates [3].

Unique electrical, optical, and magnetic properties as well as excellent chemical stability of NiO films enabled employing them in various electronic devices such as electrochromic displays, chemical sensors, solar cells, and GaN-based field-effect transistors (FET). Wider implementation of NiO films in the industry stimulates a growing demand to develop production NiO technologies. Among chemical and physical vapor deposition methods used for fabrication of p-type NiO films, reactive magnetron sputtering has demonstrated the best results. Therefore, in this communication, we describe important features of the NiO sputter technique and report NiO film properties achieved at OEM Group using traditional, well-known sputter tools suitable for mass production of compound semiconductor devices. Low sheet resistance, its uniformity across the wafer, high deposition rate and simultaneously low process temperature enabling, if necessary, NiO growth on the wafers covered with a patterned photoresist were considered as main success criteria.

200-nm-thick NiO films were deposited on 4” thermally oxidized Si wafers by RF reactive magnetron sputtering in pure oxygen atmosphere using MRC Eclipse Mark IV sputter tool equipped with a flat magnetron RMX-12 having rotating magnetic array. RF generator was connected through the matching network to the 12” diameter sputtering target produced of pure (99.99%) nickel oxide. Process chamber was pumped down by a cryo pump, base vacuum was 3E-8 Torr. Electrically isolated contact type wafer holding mechanism with backside gas flow was used to keep wafer temperature below 70°C during deposition. Target to wafer distance was 2.5”. For process optimization, sputter parameters varied in the following limits: RF power = 1-2 kW; Ar flow = 0-50 sccm; O_2 flow = 10-50 sccm; gas pressure = 2-9 mTorr.

As expected, NiO films deposited in pure Ar atmosphere were translucent and highly resistive (R_s = 50-100 kΩ/sq), while addition of O_2 to sputter gas enabled reducing the resistance drastically. With addition O_2 to Ar, the film transmittance reduced too indicating that oxygen-rich films are p-type NiO. Deposition in pure O_2 led to further lowering R_s down to 3 kΩ/sq. Higher RF power (2 kW) and lower O_2 pressure (3 mTorr) were beneficial to minimize R_s.

X-ray Theta-2Theta scans of the films deposited in Ar-O_2 gas mix did not elicit diffraction peaks related to NiO phases indicating amorphous or nanocrystalline structure. When the film was deposited in pure O_2 at relatively high pressure (8 mTorr), a wide diffraction peak appeared at 2Theta = 42.3° corresponding to NiO (200) reflection - so called bunsenite. The NiO (200) peak became stronger and narrower when films were deposited at lower O_2 pressure of 3-4 mTorr (Fig. 1). Increasing sputter power from 1 to 2 k W increased deposition rate to 16 nm/min and improved R_s uniformity across the wafer. R_s distribution became smoother and more consistent from point to point with 3σ uniformity less than 4%. Those films had smooth surface with RMS = 1.3 nm and smaller grains (Fig. 2) compared to the films deposited in Ar-O_2 mix. All oxygen-rich NiO films deposited in pure O_2 had compressive stresses in the range of 1-1.5 GPa.

We found that sheet resistance of p-type NiO films is not directly reversal proportional to film thickness. Although R_s of thinner film is higher than R_s of relatively thick film, its value is actually lower than it would be expected based on Ohm's Law. Since mechanism of p-type conductivity in NiO films deals with structural defects, such as excessive oxygen atoms in interstitial positions and Ni vacancies in the lattice, it is reasonable to conclude that lower specific resistance (ς) in thinner NiO films is due to higher defect concentration, which is inherent to initial steps of polycrystalline film growth. Development of more thorough grain structure in thicker films leads to lower defect level and hence higher ς.

It is necessary to point out that specific feature of reactive sputtering of p-type NiO films was poor R_s repeatability from wafer to wafer: film on the first wafer deposited in a "cold" tool had highest R_s, which then gradually reduced from film to film on the following wafers. Therefore, an additional investigation was performed to clarify the root reason of this phenomenon. We found that about 30-minute target pre-sputtering in O_2 atmosphere is required to stabilize the film resistance and to get a smooth R_s distribution across the wafer. The conditioning phenomenon can be explained with a conjecture that chemical composition of the NiO target surface is modified after long operation in oxygen plasma of RF discharge, which leads to dynamically sustaining oxygen saturation in the near surface region. This model is in a good agreement with the observation that the effect of target conditioning was not preserved for a long period of time. The film deposited after one hour delay exhibited higher resistance again because that module idle time was enough for realizing the excessive oxygen from the target.

One more interesting phenomenon was discovered as a result of periodic maintenance of the process chamber. The very first NiO films deposited right after the module was pumped down from atmosphere had much lower resistance than the films subsequently deposited later after better vacuum restoration in the chamber. Low R_s values (<1 kΩ/sq) were repeatedly obtained every time, when the module was vented to atmosphere. This phenomenon can be understood, if recollect that the first ionization potential of H_2O vapor (12.61 eV) is remarkably lower than the potential of O_2 (13.618 eV). Due to dissociation of residual water molecules in RF discharge, more active oxygen species (compared to neutral oxygen), such as oxygen radicals and/or ions, are released into the process chamber and participate in plasma-chemical reactions. These species can efficiently interact with the growing NiO film and create more oxygen interstitials in the film structure responsible for stronger p-type conductivity. These results can be used for further enhancement of p-type conductivity in the NiO films by addition of a small amount of water vapor into the gas mix during sputtering.

In conclusion, we have developed the RF magnetron reactive sputtering process ensuring growth of low-resistive p-type NiO thin films (R_s < 3 kΩ/sq; ς < 0.05 Ω-cm) with high deposition rate and repeatability from wafer to wafer, and exhibiting smooth surface and strong (200) texture suitable for implementation into mass production of FET and other semiconductor devices.

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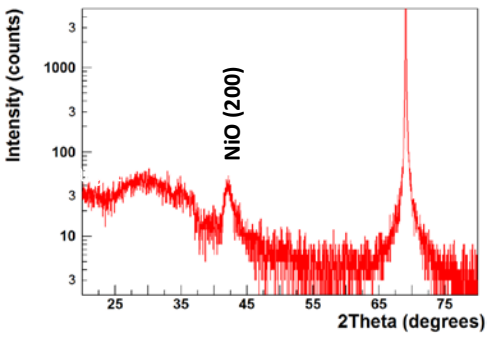

Fig. 1. X-ray diffraction patterns of 200-nm-thick NiO film deposited with RF power 2 kW in pure oxygen at pressure 3 mTorr.

Fig. 2. AFM micrograph of NiO film (scan area 10x10 μm) deposited in pure oxygen. Surface roughness RMS = 1.3 nm.