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

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Abstract

An MRC Eclipse Mark IV sputter tool, which is widely used in mass production of compound semiconductor devices, was employed for reactive RF magnetron sputtering of 200-nm thick oxygen-reach NiO films in a pure oxygen atmosphere. Low-resistive p-type NiO thin films with sheet resistance less than 3 kΩ/sq exhibiting a smooth surface and a strong NiO (200) texture were reproducibly grown on thermally oxidized Si wafers at near-room temperature. Film properties versus sputter conditions and some important features of the NiO film processing are discussed, such as the resistance aging phenomenon, the film resistance repeatability from wafer to wafer, and the growth of abnormally low-resistive films.

INTRODUCTION

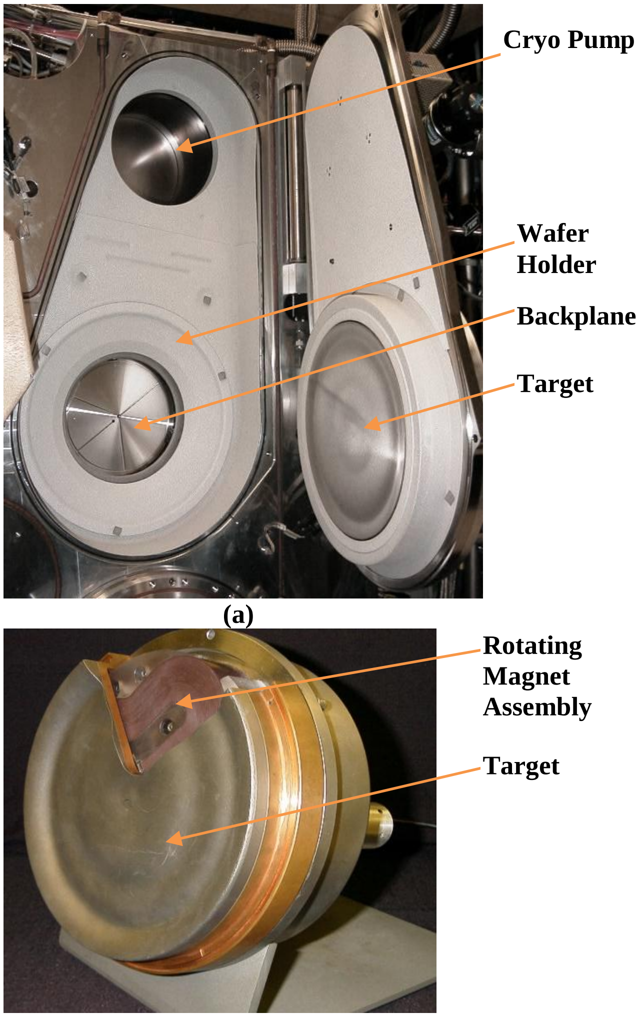
Non-stoichiometric nickel oxide (NiO) thin films can exhibit p-type semiconducting properties and possess a wide band gap (3.6-4.0 eV) and simultaneously low electrical resistance, when film growth conditions lead to generating nickel vacancies and/or forming interstitial oxygen atoms in NiO crystallites [1, 2]. It was shown that resistivity of the films deposited by radio-frequency (RF) reactive magnetron sputtering in an Ar-O_2 gas mix decreased as oxygen partial pressure increased. Films with the lowest resistivity can be obtained when sputtered from a NiO target in a pure oxygen atmosphere on unheated substrates [3]. Deposition in O_2 leads to oxygen enrichment in the NiO lattice and appearance of Ni vacancies creating holes to produce p-type conductivity [4].

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, resistance uniformity across the wafer, high deposition rate and simultaneously low process temperature enabling NiO growth on the wafers covered, if necessary, with a patterned photoresist were considered as main success criteria.

SPUTTER EQUIPMENT AND PROCESS CONDITIONS

200-nm-thick NiO films were deposited on 100-mm diameter thermally oxidized Si wafers having 500-nm-thick oxide layer. An MRC Eclipse Mark IV sputter tool (Fig. 1) equipped with an RMX-12 magnetron having a flat round sputtering target and rotating magnetic array (Fig. 2) was employed for reactive magnetron sputtering of NiO films in an Ar-O_2 gas mix as well as in a pure oxygen atmosphere. The RF generator (13.56 MHz) was connected through the matching network to the 300-mm diameter target fabricated of pure (99.99%) nickel oxide. The process chamber was cryogenically pumped to a base vacuum of 3E-8 Torr. An electrically isolated, contact type wafer holding mechanism with backside gas flow was used to keep wafer temperature below 70°C during deposition. The target to wafer distance was 63 mm.

Fig. 1. MRC Eclipse Mark IV sputter tool equipped with plasma pre-clean chamber and three sputter chambers.



(a)

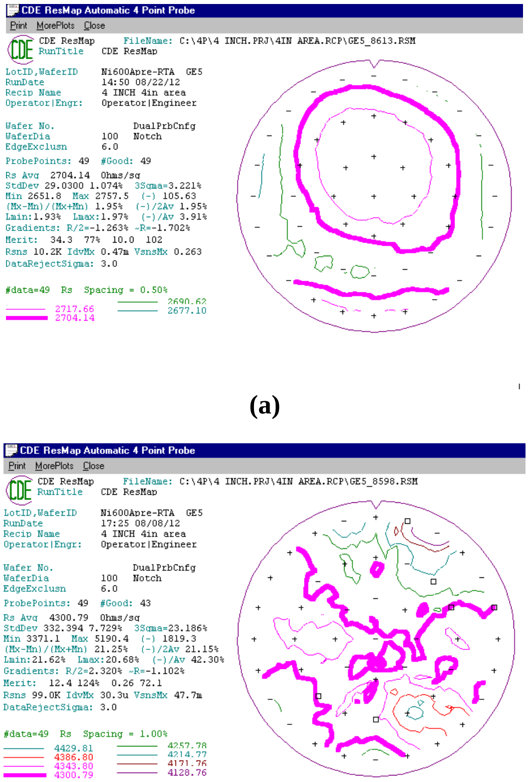
(b)

Fig. 2. MRC Eclipse Mark IV: (a) sputter process chamber and (b) magnetron RMX-12.

For process optimization, sputter parameters varied in the following limits: RF power = 1-2 kW; Ar gas flow = 0-50 sccm; O_2 gas flow = 10-50 sccm; total gas pressure = 2-9 mTorr; sputter duration = 600-1920 s. High Ar flow of 100 sccm was employed during the first 10 s of the sputter process for the reliable plasma ignition in the magnetron. During the entire film growth process, the wafer was not biased and received a floating potential from plasma discharge. In some experiments, RF plasma etch was employed for wafer pre-clean using an inductively coupled plasma source (ICP) with the following process parameters: Ar gas flow = 25 sccm; accelerating voltage = 100 V; ICP power = 800 W; etch duration = 15 s.

SPUTTERING IN ARGON AND ARGON-OXYGEN GAS MIX

As expected, NiO films deposited in a pure Ar atmosphere were translucent and highly resistive, so their sheet resistance R_s could not be measured by a 4-point probe. Adding O_2 to the sputter gas enabled reducing the film resistance remarkably. Besides lowering the electrical resistance with increasing the O_2 content in the gas mix, the film transmittance reduced too, indicating formation of oxygen-rich p-type semiconducting films, which absorb incident light due to the high concentration of the oxygen interstitial atoms [3]. However, all films produced with O_2 flows in the range of 10-50 sccm remained relatively highly resistive with an average R_s of 50-100 kΩ/sq and a non-uniform R_s distribution across the wafer (up to 50-70% in terms of 3σ) until Ar gas flow was reduced from the normally used in the RMX-12 magnetron 25-50 sccm to less than 10 sccm. Gradual diminishing both the Ar content in the gas mix and the total gas pressure resulted in reducing the R_s below 10 kΩ/sq and improving the R_s uniformity.



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Operator|Engr:      Operator|Engineer

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EdgeExclusn         6.0
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Rs Avg  2704.14  Ohms/sq
StdDev 29.0300 1.074%  3Sgma=3.221%
Min 2651.8  Max 2757.5  (-) 105.63
(Mx-Mn)/(Mx+Mn) 1.95%  (-)/2Av 1.95%
Lmin:1.93%  Lmax:1.97%  (-)/Av 3.91%
Gradients: R/2=-1.263% ~R=-1.702%
Merit:  34.3  77%  10.0  102
Rsns 10.2K IdvMx 0.47m VsnsMx 0.263
DataRejectSigma: 3.0

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         2704.14
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(a)

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StdDev 332.394 7.729%  3Sgma=23.186%
Min 3371.1  Max 5190.4  (-) 1819.3
(Mx-Mn)/(Mx+Mn) 21.25%  (-)/2Av 21.15%
Lmin:21.62%  Lmax:20.68%  (-)/Av 42.30%
Gradients: R/2=2.320% ~R=-1.102%
Merit:  12.4 124%  0.26 72.1
Rsns 99.0K IdvMx 30.3u VsnsMx 47.7m
DataRejectSigma: 3.0

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         4386.80          4214.77
         4343.80          4171.76
         4300.79          4128.76
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(b)

Fig. 3. 4-point probe sheet resistance maps of the NiO film deposited with RF power 2 kW in pure O_2 atmosphere at low process pressure: (a) as-deposited and (b) after exposure to air for 60 days.

SPUTTERING IN PURE OXYGEN

Deposition in pure O_2 led to further lowering R_s down to 3 kΩ/sq (Fig. 3a). Higher RF power (2 kW) and lower O_2 gas flow (15 sccm) and process pressure (3-4 mTorr) were beneficial to minimize R_s.

X-ray Theta-2Theta scans of the films deposited in an Ar-O_2 gas mix did not elicit diffraction peaks related to NiO phases indicating amorphous or nanocrystalline structure (Fig. 4a). 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 inherent to so called bunsenite structure. The NiO (200) peak became stronger and narrower when films were deposited at lower O_2 pressure of 3-4 mTorr (Fig. 4b).

Increasing sputter power to 2 kW was beneficial for both the sputter process yield due to increasing deposition rate to 16 nm/min and for the overall film quality due to improving R_s uniformity across the wafer. The R_s distribution became smoother and more consistent from point to point with 3σ uniformity less than 4%. Those films had smooth surfaces with RMS = 1.3 nm and smaller grains (Fig. 5b) compared to the films deposited in an Ar-O_2 gas mix (Fig. 5a).

All oxygen-rich NiO films deposited in pure O_2 had higher compressive stresses (in the range of 1-1.5 GPa) compared to the films deposited in an Ar-O_2 mix (in the range of 0.5-0.8 GPa).

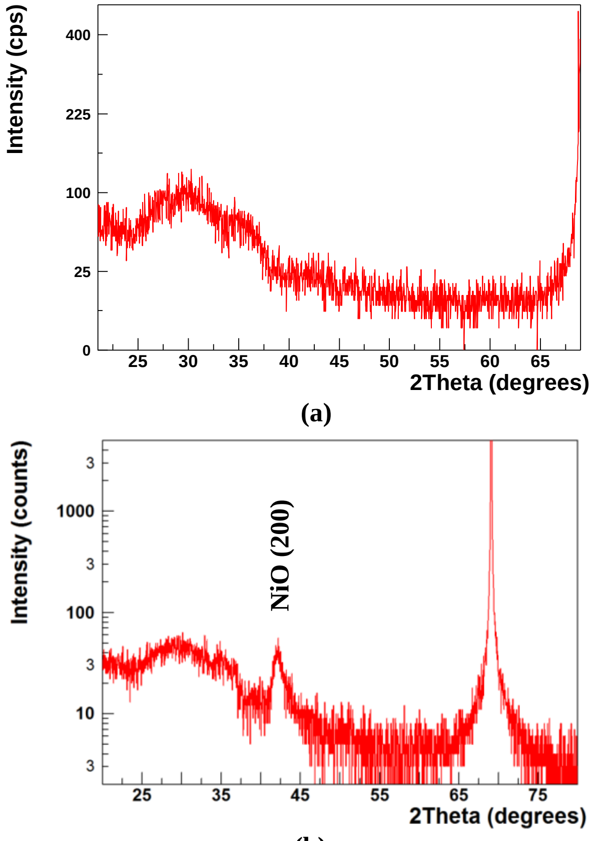

Fig. 4. X-ray diffraction patterns of 200-nm-thick NiO films deposited with RF power 2 kW: (a) in Ar-O_2 gas mix and (b) in pure O_2 at process pressure 3 mTorr.

SOME SPECIFIC FEATURES OF NiO FILM PROCESSING

It is necessary to point out that NiO films experience degradation of sheet resistance and resistance distribution across the wafer during exposure to air. For instance, the as-deposited in pure O_2 film had an average resistance of 2700 Ω/sq and 3σ uniformity of 3.2% (Fig. 3a). After exposure to air for 60 days, its R_s increased to 4300 Ω/sq and uniformity worsened to 23% (Fig. 3b). X-ray Theta-2Theta scans showed no change in the preferred orientation in (200) direction, so the film preserves its bunsenite-like structure. According to results published in [5], the electrical aging phenomenon is attributed to the adsorption of H_2, CO, and H_2O molecules on the NiO surface leading to injection of electrons into the film, which lowers the holes' concentration in the p-type NiO and thereby reduces the film conductivity. To preserve the film quality, it is necessary to store the as-deposited wafers in vacuum or in dry Ar environment.

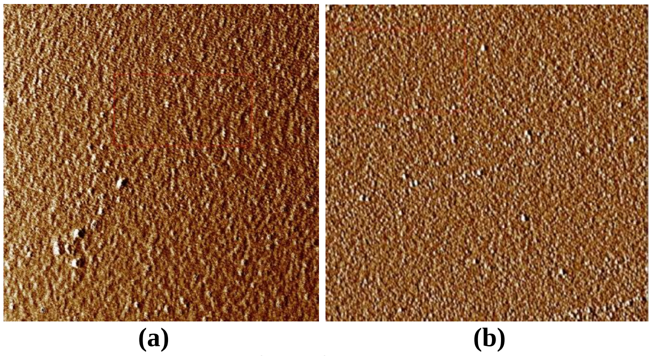

Fig. 5. AFM micrographs of NiO films deposited (a) in Ar-O_2 gas mix (surface roughness RMS = 2.5 nm) and (b) in pure oxygen (RMS = 1.3 nm). Scan area 10x10 µm.

We found that sheet resistance of as-deposited NiO films is not strictly inversely-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 would be expected based on Ohm's Law. Since the 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 bulk resistance (also called specific resistance or resistivity, ς) in thinner NiO films is due to higher defect concentration, which is inherent to the initial steps of polycrystalline film growth. Development of more thorough grain structure in thicker films leads to lower defect level and hence higher ς.

A 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 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.

CONCLUSION

An industrial RF magnetron sputtering process ensuring growth of low-resistive p-type NiO thin films has been developed using a well-known production sputter tool such as an MRC Eclipse Mark IV. Sputtering the NiO target in a pure oxygen atmosphere at near-room wafer temperature enabled the films exhibiting remarkably lower resistivity than previously published results ($\varsigma < 0.05$ Ω-cm for 200-nm thick films), a smooth surface, and a strong NiO (200) crystallographic texture. The sputter process at 2 kW of RF power and 3-4 mTorr of O_2 pressure demonstrated high deposition rate of 16 nm/min, good sheet resistance uniformity, and repeatability from wafer to wafer, suitable for implementation into the mass production of FET and other semiconductor devices.

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ACRONYMS

MRC: Material Research Corporation
RF: Radio Frequency
FET: Field-Effect Transistors
AFM: Atomic Force Microscopy
RMS: Root Mean Square
ICP: Inductively Coupled Plasma