Growth, physical and electrical characterization of nickel oxide thin films prepared by plasma-enhanced atomic layer deposition using nickelocene and oxygen precursors

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Keywords: atomic layer deposition, nickel oxide, nano-films

Abstract

Nickel oxide (NiO) thin films are prepared by plasma-enhanced atomic layer deposition using nickelocene (NiCp2) and oxygen (O2) precursors. The effects of process parameters on the growth rate of NiO film are investigated, including deposition temperature, NiCp2 pulse time, and O2 plasma pulse time. In terms of deposition temperatures between 225 and 275 °C, a stable growth rate of \( \sim 0.17 \text{ Å/cycle} \) is obtained, meanwhile, the deposited films contain Ni(II)–O, Ni(III)–O, Ni(II)–OH, C–C bonds and metallic Ni atoms, and exhibit a smooth surface with root-mean-square roughness of \( \leq 0.37 \text{ nm} \). As the deposition temperature increases from 150 to 350 °C, the deposited NiO film changes from an amorphous state to a NiO (200) orientation-dominated texture and further to NiO (111) and (200) orientations concomitant polycrystalline one; at the same time, the transmittance of the film shows a decline tendency, and the optical band gap decreases from 3.69 to 3.48 eV. Furthermore, it is found that the deposited NiO film behaves like a dielectric rather than a semiconductor, and for the NiO film deposited at 250 °C, a dielectric constant of 16.7 is demonstrated together with a film composition of 51.6% Ni, 40% O and 8.4% C.

1. Introduction

Nickel oxide (NiO) has a wide band gap (~3.6 eV), high transmittance in the visible range and an excellent chemical stability; it is thus widely used in electronic devices [1], solar cells [2, 3], super-capacitors [4, 5], gas sensors [6–8], catalysis [9, 10] and so on. So far, most NiO thin films have been prepared by magnetron sputtering [11–13], chemical solution [14, 15], thermal oxidation [16], and atomic-layer-deposition (ALD) [2, 4, 5]. In terms of our interested electronic and photovoltaic device field, high quality thin films with good uniformity across a large area, excellent step coverage and atomic scale thickness controllability are strongly required especially for nanoscale devices. However, both magnetron sputtering and chemical solution methods are hard to achieve a large area film uniformity and precise thickness controllability. The thermal oxidation preparation of NiO films requires a high processing temperature of 400 °C [16], which limits its application in the field of transparent flexible electronics. As an emerging preparation technology of nanoscale thin films, the ALD technique relies on self-limiting chemical reactions on a substrate surface, which is realized by alternately importing a precursor into a reaction chamber and a sufficient purging step between two precursor pulses. Therefore, it can ensure precise control of atomic-scale thickness, a large area uniformity and excellent step coverage [2, 4, 17], and has been widely used in the microelectronic industry.

Till now, various precursors have been reported for thermal ALD of NiO thin films, including Nickelocene (NiCp2)/O3 [18–20], nickel ethylcyclopentadienyl (Ni(EtCp)2)/O3 [19, 21], nickel(ii) 1-dimethylamino-2-methyl-2-propanolate (Ni(dmamp)2)/H2O [22], nickel bis(alkylamidinate) (Ni(amd))/H2O [23] and nickel bis (N,N′-di-tert-butylacetamidinate) (Ni(Bu-MeAMD)2)/H2O [2]. Nevertheless, to the best of our knowledge, few researchers utilized plasma-enhanced ALD to grow the NiO thin films. In addition, most of investigators still
focused on morphological, optical and chemical characterization of ALD NiO films, and none was involved in electrical characterization of ALD NiO films.

In this article, we used a much cheaper Ni precursor, i.e., NiCp2, in comparison with Ni(dmamp)2 and Ni(amd)2 [9]. Meanwhile, O2-plasma with high oxidizability was adopted as an oxygen source, which could reduce the deposition temperature of NiO films. Therefore, the NiO thin films were successfully grown by plasma-enhanced ALD (PEALD) using the precursors of NiCp2 and O2, and the effects of process parameters on the growth rate, film texture, chemical composition, optical and electrical properties of NiO films were investigated comprehensively. In particular, the electrical characteristics of the NiO films were investigated for the first time by multi-methods.

2. Experimental details

2.1. Sample preparation

2.1.1. Deposition of NiO films

NiO films were deposited on cleaned silicon and quartz glass substrates by PEALD (R200 Advanced, Picosun), respectively. It is worthwhile to mention that the silicon wafers were cleaned using a standard RCA process, and the quartz glass was ultrasonically cleaned with acetone and isopropanol. NiCp2 was used as the Ni precursor, whose container was kept at 80 °C in order to obtain a sufficient vapor pressure. The gaseous NiCp2 was transported into the reaction chamber by a high purity N2 carrier gas with a flow rate of 50 sccm. The remote O2 plasma was used as a co-reactant, which was produced by an inductively-coupled plasma (ICP) generator under the following conditions: a RF power of 2000 W, a working pressure of 9.5 × 105 Pa, an Ar flow rate of 50 sccm, and a O2 flow rate of 200 sccm. During the film growth, the working pressure was maintained at 1100 Pa in the deposition chamber, and the deposition temperature was varied from 150 to 350 °C in order to get an ideal process window. One deposition cycle includes a pulse of NiCp2, 10 s of N2 purging to remove the residual precursor and byproducts, a pulse of O2-plasma, and 10 s of N2 purging in sequence, in which the pulse times of NiCp2 and O2 plasma were optimized, respectively.

2.1.2. Fabrication of TaN/Al2O3/NiO/TaN structures

Firstly, Ta (100 nm)/TaN (20 nm) bi-layers were sequentially deposited on a 300 nm SiO2 film-coated silicon substrate by magnetron sputtering, which served as a bottom electrode. Then, bilayer films of Al2O3 (28 nm)/NiO (15 nm) were successively deposited by thermal ALD and PEALD, respectively. Finally, TaN top electrodes with a thickness of 140 nm and a diameter of 98 μm were formed by photo-lithography and a lift-off process.

2.1.3. Fabrication of Au/NiO/p-Si (MOS) capacitors

An around 10 nm NiO film was grown on a p-type silicon substrate (1 × 10Ω·cm) as a dielectric layer by PEALD at 150, 250 and 350 °C, respectively. Then, Au electrodes with a thickness of 50 nm and a diameter of 98 μm, which were deposited by thermal evaporation, were formed on the NiO film by photo-lithography and a lift-off process.

2.2. Characterization of the samples

The film thickness was measured by x-ray reflection (XRR), and the texture of the deposited film was characterized by x-ray diffraction (XRD), both of them were performed on x-ray diffractometer (Bruker D8 Discover) with Cu Kα radiation. The film surface morphologies were observed with atomic force microscopy (AFM) (Bruker Icon). The elemental composition and chemical bonds of the film were analyzed via x-ray photoelectron spectroscopy (XPS), which was measured on a x-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with Al Kα radiation (1486.6 eV). The pass energies of 160 eV and 40 eV were adopted for survey and high-resolution XPS spectra, respectively. The charging effect was compensated by a in situ low energy electron gun during the XPS measurements, and then was calibrated by using C1s = 284.8 eV as a reference. The energy of argon ions was kept at 2 keV for in situ surface etching. The transmittance of the film was characterized using UV–vis NIR spectrophotometer (Lambda 950). The current density–electric field (J–E) and capacitance-voltage (C–V) characteristics of the samples were measured using a semiconductor device analyzer (Agilent Tech B1500A) and a precision impedance analyzer (Agilent 4294 A), respectively. The cross-section of the MOS capacitor was observed by high resolution transmission electronmicroscopy (HRTEM) (FEI Talos F200X).
3. Results and discussion

3.1. Growth characteristics of NiO films

Figure 1(a) shows the growth rate of the PEALD film as a function of deposition temperature while keeping NiCp₂ and O₂ plasma pulse times at 3 and 30 s, respectively. It is found that a stable growth rate of ~0.17 Å/cycle can be obtained between 225 and 275 °C, which is called as the temperature window of the ALD process. When the deposition temperature is lower than 225 °C, the growth rate becomes larger in comparison with those in the range of 225 ~ 275 °C. This is because the adsorption of NiCp₂ on the substrate surface outperforms its desorption at lower substrate temperatures, hence resulting in condensation of NiCp₂ on the substrate [24]. When the substrate temperature is higher than 300 °C, a much higher growth rate is observed. This is due to thermal decomposition of NiCp₂ at higher temperatures, hence leading to deposition of non-volatile substances on the substrate surface [25].

In order to investigate the effect of NiCp₂ pulse time on the growth rate of the film, the other process parameters of substrate temperature and O₂ plasma time are fixed at 250 °C and 30 s, respectively. As shown in figure 1(b), when the pulse time of NiCp₂ is extended from 0.5 s to 2 s, the growth rate gradually increases from ~0.07 to 0.17 Å/cycle, followed by a relatively stable growth rate as a function of NiCp₂ pulse time. This indicates that around 2 s of NiCp₂ pulse can generate a saturated surface reaction, and thus the growth rate is not affected by further increasing the pulse time of NiCp₂ because of the self-limiting growth characteristic of ALD. A similar phenomenon is also observed for the O₂-plasma pulse time dependent film growth rate while fixing substrate temperature and NiCp₂ pulse time at 250 °C and 3 s, respectively, as shown in figure 1(c). As the O₂-plasma pulse time increases from 10 s to 30 s, the growth rate increases gradually. When the O₂-plasma pulse time exceeds 30 s, the film growth rate approaches a saturation value of ~0.17 Å/cycle. Furthermore, the thickness of the deposited film exhibits a linear rise with increasing the deposition cycles under 3 s NiCp₂ pulse, 30 O₂ plasma pulse and 250 °C substrate temperature, as shown in figure 1(d). This reveals that the film growth conforms to the rule of ALD, and the film thickness can be precisely controlled by deposition cycles. In addition, based on the intersection between the fitted line and the x-axis, it can be inferred that an initial incubation period of 6 cycles exists during PEALD of NiO on a cleaned Si substrate. In brief, based on the aforesaid experimental results, the ideal process parameters for the NiO film should be as follows: a deposition temperature range of 225 ~ 275 °C, NiCp₂ pulse time of 2 s, O₂ plasma pulse time of 30 s, and N₂ purging time of 10 s.
3.2. Physical characterization of the NiO films

Figure 2 shows the XRD patterns of the NiO films (around 20 nm) deposited at different temperatures. It can be seen that no diffraction peak appears for the NiO film deposited at 150 °C, which indicates that the deposited NiO film is amorphous. This is because such a low deposition temperature cannot offer enough activation energy for the reaction between NiCp2 and O2 plasma, hence resulting in incomplete reaction (i.e., condensation of NiCp2) and incorporation of carbon-based impurities. When the deposition temperature is raised to 200 °C, the deposited film shows a diffraction peak at 2θ = 43.2°, corresponding to the NiO (200) orientation. Further, when the growth temperature is increased to 250 °C, an additional tiny diffraction peak associated with the (111) orientation appears at 2θ = 37.2° [14, 26, 27]. Interestingly, when the deposition temperature rises to 300 °C or higher, the diffraction peak of NiO (111) becomes intense, however, the diffraction peak of NiO (200) weakens. The aforementioned results indicate that the preferential orientation of the deposited NiO film gradually transforms from (200) to (111) orientation with increasing the deposition temperature. This can be understood as follows [28, 29]. As the deposition temperature increases, the surface reactivity of the reactant species is enhanced, thus promoting the nucleation and growth of NiO grains. On the other hand, the crystallographic texture of the NiO film is usually affected by the arrangement of O2− [28]. Compared with lower substrate temperatures (e.g., 200 and 250 °C), higher substrate temperatures (e.g., 300 and 350 °C) can allow the oxygen species arriving at the substrate surface to gain enough thermal energy to activate themselves; that is to say, active oxygen species become relatively sufficient at higher substrate temperatures [29]. In this case, the (111) plane is the most densely packed plane of O2− among the planes composed of both Ni2+ and O2− for a NiO crystal structure, hence resulting in the formation of a (111) -texture due to minimization of the surface free energy [28, 29]. However, under the condition of insufficient active oxygen species at the lower substrate temperatures, the (200) plane is the most densely packed plane, thus producing a (200) -texture [28, 29].

The surface morphologies of the NiO films (around 20 nm) deposited at different temperatures were measured by AFM. It is found that the film surface becomes rougher and rougher with increasing deposition temperature from 150 to 350 °C, as shown in figures 3(a)–(c). Further, the root-mean-square (RMS) roughness of the film is plotted as a function of deposition temperature, shown in figure 3(d). As the deposition temperature ascends from 200 to 275 °C, the RMS roughness of the NiO film exhibits a slow increase from 0.24 to 0.37 nm. By comparison with the amorphous NiO film deposited at 150 °C (RMS = 0.23 nm), this might be related to the growth of grains because a high substrate temperature can enhance the mobility and activity of atoms. Nigro et al also reported that a higher deposition temperature resulted in the formation of larger grains in the NiO film deposited by metal organic chemical vapor deposition [30]. When the substrate temperature exceeds 275 °C, the NiO film shows a distinct increase in RMS roughness. This should be dominated by random deposition of nonvolatile substances incurred by thermal decomposition of NiCp2.

It is well known that the sample surface is usually contaminated during transfer of the sample. To avoid the influence of the surface contaminants on the chemical composition of the sample during XPS measurements, the sample surface should be etched by in situ Ar ion bombardment till complete removal of the surface contaminants. Figure 4 illustrates an evolution of the XPS survey spectrum of the deposited film at 150 °C as a function of in situ Ar ion etching. In terms of the virgin film, the photoelectron peaks of Ni 2p, C 1s and O 1s are
clearly observed. After Ar ion etching for 60 s, the C 1s peak intensity decreases significantly, and the Ni 2p peak becomes intense remarkably. As the etching time lengthens to 90 s, these photoelectron peaks do not show discernable changes. From the extracted atomic percentages listed in figure 4, it is seen that the elemental compositions are stable in the film when the etching time reaches 60 s. This indicates that a much higher C content for the virgin film should originate from adventitious contamination, which can be fully removed by 60 s etching. Therefore, to obtain the intrinsic composition of the deposited film, all the samples were etched with 60 s in situ Ar ion bombardment for the XPS measurements. Table 1 lists the elemental percentages of the NiO films grown at 150, 250, and 350 °C, respectively. Compared to a lower or higher deposition temperature (150 or 350 °C), a deposition temperature (e.g., 250 °C) in the process window can attain a higher purity of NiO with a minimum carbon content of 8.4%. This is because the deposition temperatures in the process window can provide the ALD reaction with enough activation energy, which makes the Ni–Cp bonds easily break,
resulting in a decrease of carbon residuals in the deposited film. Nevertheless, when the deposition temperature is raised to 350 °C, the content of C increases again, even to 14.4%. This should be related to thermal decomposition of the ligand on the surface, leading to incorporation of more carbon residuals into the film [25, 31, 32]. In terms of 250 °C within the optimized process temperature window, the resulting NiO film contains 51.6% Ni, 40% O and 8.4% C.

In order to investigate the effect of deposition temperature on chemical bonds of the deposited film, high-resolution of C 1 s, O 1 s and Ni 2p3/2 XPS spectra were analyzed by the software ‘casaXPS’. The Shirley-type background and baseline were treated automatically by the software. During each sub-peak fitting, the Gauss-Lorentz function was used; meanwhile, the constrain on the peak position was set in the range of −0.2 eV ∼ + 0.2 eV, and the full-width-at-half-maximum (FWHM) of each sub-peak was set at ” ± 2 eV. Figure 5 shows the high-resolution C 1 s XPS spectra of the NiO films grown at different temperatures. It is found that all the NiO films show an obvious peak at 284.8 ± 0.2 eV, which should be attributed to C–C bonds [4, 33]. Furthermore, one intense peak is observed at 289.8 ± 0.2 eV for the film deposited at 150 °C, which comes from oxycarbide groups such as alcohols, carboxylic acid, etc [34, 35]. When the deposition temperature increases to 250 °C, the peak becomes very small, and disappears at the deposition temperature of 350 °C. This reveals that a high deposition temperature can restrain the formation of the oxycarbide. In addition, under the deposition temperature of 350 °C, the peak associated with C–C bonds heightens significantly. This should be ascribed to the decomposition of NiCp2 molecules, leading to the formation of the byproducts (C5H5, C10H10 and NiC5H5) [36]. These byproduct molecules could be partially adsorbed on the substrate surface and react with the oxygen plasma, thus leading to complete dehydrogenation of them and then yielding graphite-like carbon (C–C bonds) [31].

![Figure 5. High resolution C 1 s XPS spectra of the NiO films deposited at different temperatures.](image)

Table 1. Elemental percentages in the NiO films grown at different temperatures.

| Temperature (°C) | C (at%) | Ni (at%) | O (at%) |
|------------------|---------|----------|---------|
| 150              | 14.2    | 42.2     | 43.6    |
| 250              | 8.4     | 51.6     | 40.0    |
| 350              | 14.4    | 47.9     | 37.7    |

Figure 6 shows the high resolution O 1 s XPS spectra of the NiO films grown at different temperatures. Regarding the deposition temperature of 150 °C, the O1s spectrum can be divided into four peaks, corresponding to Ni(II)–O bond (529.6 ± 0.2 eV) [1, 2], Ni(III)–O bond (531.1 ± 0.2 eV) [15, 27, 37], Ni(II)–OH bond (531.8 ± 0.2 eV) [38] and O–C=O bond (533.7 ± 0.2 eV) [39], respectively. The presence of a large number of Ni(II)–OH bonds, which account for 55.4% of the total oxygen content, reveals that such a low deposition temperature easily produces hydroxylated nickel oxide [40]. In terms of the NiO film deposited at

![Figure 6. High resolution O 1 s XPS spectra of the NiO films deposited at different temperatures.](image)
250 °C, the resulting O 1s spectrum is well separated into three peaks, corresponding to Ni(II)−O and Ni(III)−O and Ni(II)−OH bonds, respectively. The component of Ni(II)−O is dominated in the film, accounting for 78.8%. It is worth noting that the Ni(II)−OH component shows an outstanding decrease and the O−C=O component disappears. This indicates that both hydroxyl groups and oxy-carbide easily desorb from the NiO film during ALD at a higher temperature of ≥250 °C. When the deposition temperature is raised to 350 °C, the relative content of Ni(II)−O further increases to 87.2%, and those of Ni(III)−O and Ni(II)−OH decrease to 8.5% and 4.3%, respectively.

Figure 7 shows the high resolution Ni 2p$_{3/2}$ XPS spectra of the NiO films grown at different temperatures. All the Ni 2p$_{3/2}$ spectra can be well decomposed into four peaks, which are associated with Ni−Ni bonds (852.6 ± 0.2 eV) [25], Ni(II)−O bonds (854.0 ± 0.2 eV) [2, 13, 37], Ni(III)−O bonds (855.6 ± 0.2 eV) [2, 13, 37] and Ni(II)−OH bonds (856.1 ± 0.2 eV) [41, 42], respectively. By comparing the Ni 2p$_{3/2}$ spectra of the NiO films deposited at different temperatures, it is found that the component of hydroxylated nickel, Ni(II)-
Since NiO is a direct bandgap material, the transmittance of the NiO film deposited at different temperatures, the corresponding optical transmission spectra are shown in figure 8. As the deposition temperature rises from 150 °C to 350 °C, the transmittance of the deposited NiO film gradually decreases in the visible light range of 390 ~ 770 nm. This could be ascribed to two reasons. First, the content of Ni\(^{3+}\) ions in the NiO film exhibits a tendency of increase at higher deposition temperatures (see figure 7). Since Ni\(^{3+}\) ions act as color centres in nickel oxide films, the increase in the content of Ni\(^{3+}\) leads to a decrease in the transmittance of the NiO films deposited at higher temperatures. Second, the content of metallic Ni atoms (Ni\(^{0}\)) exhibits a significant rise with increasing the deposition temperature (see figure 7). Since excess metallic Ni can scatter photons, increasing the deposition temperature also can reduce the transmittance of the PE-ALD NiO film. More likely, the second effect is dominant in our case. In terms of the process window of 225 ~ 275 °C, the transmittance of the deposited NiO films can be up to 70%.

Further, the optical band gap (E\(_g\)) of the NiO film is determined by the Tauc’s relation:

\[
\alpha h\nu = A(h\nu - E_g)^n,
\]

where \(\alpha\) is the absorption coefficient, \(h\nu\) is the incident light frequency, \(h\) is the Planck constant, \(A\) is a constant. Since NiO is a direct bandgap material, \(n\) takes 1/2 \([13, 43]\). Further, \(\alpha\) is defined as \(-(\ln T/d)\), where \(T\) and \(d\) represent the transmittance and thickness of the film, respectively. By extrapolating the straight line portion of \((\alpha h\nu)^2\) versus \(h\nu\), its intersection with the horizontal axis corresponds to the E\(_g\) of the NiO film, as shown in figure 9(a). The deduced E\(_g\) for different NiO film is plotted in figure 9(b). As the deposition temperature increases from 150 °C to 350 °C, the E\(_g\) of the NiO film decreases from 3.69 eV to 3.48 eV. This could be ascribed to the incremental Ni-Ni component in the NiO film with increasing deposition temperature because metallic Ni doping is likely to generate some additional energy levels in the band gap, resulting in the reduction of the energy associated with the transition from valence band to conduction band. \([43–45]\)

Table 2 shows comparisons of process parameters and film characteristics of various NiO thin films prepared by different methods. It is found that the sputtering technique generates a much larger RMS roughness (5~18 nm) than the ALD technique (0.23~1.25 nm), meanwhile, the former also produces a wider atomic ratio range of Ni:O (0.45~1.86) than the latter (1.13~1.29). These data indicate that the ALD NiO film can possess a quite smooth surface and a stable elemental composition. In addition, the chemical solution method faces a higher thermal budget even up to 400 °C in comparison with both the ALD and sputtering techniques. In terms of the ALD process, the thermal ALD (T-ALD) generally leads to a larger surface roughness (e.g., RMS = 0.6~1.25 nm for 18~22 nm NiO films) \([2, 19, 46]\), however, our PE-ALD process can attain an improved film roughness, i.e., RMS = 0.23~0.37 nm for 20 nm NiO films, as well as a relatively low deposition
3.3. Electrical characterization of the NiO films

To determine the conductivity type of the NiO film, the C-V curve of the metal/Al2O3/NiO/metal structure was measured. As shown in Figure 10, all the C-V curves behave like metal-insulator-metal (MIM) capacitors [49, 50] rather than metal-oxide-semiconductor (MOS) capacitors. This indicates that the deposited NiO films can be considered as dielectrics. On the other hand, it is reported that p-type metal oxides generate holes by means of metal cation vacancies serving as acceptors [1, 14, 16, 27], in which the atomic ratio of oxygen to metal should be larger than its stoichiometric ratio (O/Ni = 1:1). In our case, the O/Ni atomic ratio is less than the stoichiometric ratio. For example, the atomic ratio of O/Ni is 0.775 for the film deposited at 250 °C. That is why the current NiO films exhibit dielectrics rather than p-type semiconductors.

Further, various MOS capacitors with different NiO deposition temperatures were fabricated and characterized electrically. In the beginning of film deposition, the Si substrate is exposed to the O2-plasma, which could generate an interface layer of SiO2. To confirm the interfacial layer thickness, the cross-section HRTEM image of a representative MOS capacitor with the 250 °C NiO dielectric is shown in Figure 11. It is found that an interfacial layer of 1 nm SiO2 is formed between the NiO film and the p-type silicon substrate.

Further, the k value of the NiO film can be deduced from the following formula:

\[
\frac{1}{C_{\text{total}}} = \frac{1}{C_{\text{SiO}_2}} + \frac{1}{C_{\text{NiO}}},
\]

where \(C_{\text{total}}\), \(C_{\text{SiO}_2}\) and \(C_{\text{NiO}}\) represent the measured maximum capacitance of the MOS capacitor, the SiO2 interfacial layer capacitance, the NiO dielectric capacitance, respectively. Figure 12(a) shows the C-V curves of the MOS capacitors with different deposition temperatures of NiO at 100 kHz, demonstrating a typical C-V characteristic of a MOS capacitor. Therefore, according to the measured maximum capacitance, the NiO film thickness, and the thickness (1 nm) and dielectric constant (k = 4) of the SiO2 interfacial layer, the calculated k values of the NiO films deposited at 150, 250 and 350 °C are equal to 7.9, 16.7 and 10.0, respectively. Cho et al also reported that the NiO film, which was grown from Ni(dmamb)2 and water at 140 °C by thermal ALD, had a k value of 11.9 [51]. For the 250 °C deposition temperature, the highest k value should be attributed to the purest NiO film, which contains the fewest C − C bonds with lower polarizability, as indicated in Table 1 and Figure 5. Figure 12(b) shows the leakage current characteristics of the MOS capacitors with different NiO dielectrics. It is seen that as the deposition temperature increases from 150 to 350 °C, the leakage current density increases gradually in the high electric field region (i.e., ~2 MV/cm). This is related to the increase in metallic Ni component of the NiO film.

4. Conclusion

In this study, NiCp2 and O2-plasma are used as the reactive precursors to deposit NiO films by PEALD. The effects of process parameters on the growth rate and characteristics of the NiO film are investigated comprehensively. Thus, the growth temperature window of 225 ~ 275 °C is obtained, which corresponds to a
Table 2. Comparisons of process parameters and characteristics of various NiO thin films prepared by different techniques.

| Deposition method | Reactants/ Precursors | Deposition temperature | Texture | RMS roughness (film thickness) | Impurity (at%) | Growth rate (Å/ cycle) | Optical band gap (eV) | Ni/O atomic ratio | References |
|-------------------|-----------------------|------------------------|---------|--------------------------------|----------------|-------------------------|----------------------|-------------------|------------|
| Magnetron sputtering | NiO2 + Ar | RT | Crystalline | 5' 18 nm (100 nm) | — | 3.45 | — | 0.45 | 0.68 | [1] |
| Magnetron sputtering | NiO2 + Ar | RT | Crystalline | — | 20 nm | 3.41 | 3.70 | 0.8 | [12] |
| Magnetron sputtering | NiO2 + Ar | RT | Crystalline | — | 20 nm | 3.41 | 3.70 | 0.8 | [13] |
| Chemical solution | Ni(NO3)2·6H2O | 200°C 400°C | Crystalline | 0.65 nm 0.99 nm (30 nm) | C | 3.7 | 5.5 | — | [14] |
| Chemical solution | Ni(OAc)2·4H2O | 150°C 350°C | Amorphous or crystalline | 0.40 nm 1.92 nm (not indicated) | — | 3.7 | 5.3 | — | [15] |
| Chemical solution | Ni(CH3COO)2·4H2O | 180°C 380°C | Amorphous or crystalline | 0.20 nm 0.26 nm (50 nm) | — | 3.65 | 3.82 | — | [16] |
| Thermal oxidation | Ni | 400°C | Crystalline | — | 20 nm | 3.28 | 3.36 | — | [17] |
| T-ALD | Ni(Bu-MeAMD)2·H2O | 200°C | Crystalline | 0.83 nm (22 nm) | C | 0.39 | — | — | [18] |
| T-ALD | NiCp2O | 300°C | Crystalline | — | 80 nm | 3.8 | — | — | [19] |
| T-ALD | Ni(dmamp)2·H2O | 100°C 160°C | Crystalline | 0.4 nm@120°C (80 nm) | C, F, Cl | 0.8 | — | — | [20] |
| T-ALD | Ni(amd)2·H2O | 175°C | Crystalline | — | 80 nm | 0.75 | — | — | [21] |
| T-ALD | Ni(tBu2DAD)2O3 | 185°C 200°C | Crystalline | 0.60 nm@200°C (18 nm) | C + N | 1.2 | 3.7 | 3.8 | 1.13 | 1.17 | [22] |
| T-ALD | NiCp2O | 200°C 300°C | Crystalline | 0.34 nm@300°C (28 nm) | (<0.2%)@200°C | 0.12 | — | 1.15 | @300°C | [23] |
| T-ALD | Ni(acac)2·O3 | 200°C 275°C | Crystalline | 0.5 nm@70°C (30 nm) | C(-12%)@300°C | 0.7 | — | 2.0 | — | [24] |
| PE-ALD | NiCp2O2 plasma | 225°C 275°C | Crystalline | 0.23 nm 0.37 nm (20 nm) | C(8.4%)@250°C | 0.17 | 3.48 | 3.69 | 1.29 | @250°C | This work |

Note: RT means room temperature; @200°C represents a deposition temperature of 200°C.
growth rate of \( \sim 0.17 \text{ Å/cycle} \). When the deposition temperature increases from 200 to 300 °C, the NiO film changes from the NiO (200) orientation-dominated texture to the NiO (200) and (111) orientations co-existed one. Meanwhile, the surface roughness of the film gradually increases with deposition temperature. The NiO films grown within the deposition temperature window contain Ni(II)–O, Ni(III)–O, Ni(II)–OH, C–C bonds and metallic Ni atoms. Both the transmittance and band gap of the film decrease with raising deposition temperature mainly due to the increase of metallic Ni component in the film. In addition, the film deposited at 250 °C has the highest dielectric constant, which is related to the lowest C content in the NiO film. The PEALD

Figure 10. Normalized C–V curves of the metal/Al₂O₃/NiO/metal structure at 100 kHz, where the NiO layer was deposited at 150 °C, 250 °C and 350 °C, respectively.

Figure 11. Cross-section HRTEM image of the MOS capacitor with the NiO dielectric deposited at 250 °C.
NiO film with high transmittance in the visible light range and a high k value could be very promising for the fields of transparent electronic devices and photovoltaic cells.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (61874029), and the National Key Technologies R&D Program of China (2015ZX02102-003).

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