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Synthesis of NiO nanowalls by thermal treatment of Ni film deposited onto a stainless steel substrate

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Abstract
Two-dimensional nanostructures have a variety of applications due to their large surface areas. In this study, the authors present a simple and convenient method to realize two-dimensional NiO nanowalls by thermal treatment of a Ni thin film deposited by sputtering onto a stainless steel substrate. The substrate surface area is supposed to be significantly increased by creating nanowalls. The effects on the nanowall morphology of the thermal treatment temperature and duration are investigated. A mechanism based on the surface diffusion of Ni^{2+} ions from the Ni base film is then proposed for the growth of the NiO nanowalls. The as-synthesized NiO nanowalls are characterized by scanning electron microscopy, energy-dispersive x-ray analysis, x-ray diffraction, transmission electron microscopy and high resolution transmission electron microscopy.

1. Introduction

As one kind of transition metal oxide, NiO has recently received a great deal of attention due to its applications in various fields such as thermal electrical devices, gas sensors, conducting electrodes, electrochromic films, solar cells and catalysis [1–8]. Nanostructured NiO has shown improved performance compared to its bulk or micro counterparts because of the increased surface to volume ratio, and therefore, considerable studies have been performed to realize nanostructured NiO [9–19]. NiO nanoparticles have been realized by the organic solvent method, water-in-oil microemulsion and thermal decomposition of the NiC_2O_4 precursor [9–11]. One-dimensional (1D) NiO nanostructures (nanowires, nanorods and nanotubes) have been synthesized by the wet chemical route, electrochemical deposition based on anodic alumina membranes, thermal decomposition of the NiC_2O_4 precursor, oxidation of NiS, thermal decomposition of the precursor deposited in $NiSO_4$ aqueous solution with urea, sol–gel method, thermal oxidation of a thin nickel foil and the template synthesis technique [12–19]. Although NiO nanoparticles and 1D NiO nanostructures have been successfully realized, there has been no report in the literature to realize two-dimensional (2D) NiO nanostructures. It is well known that 2D nanostructures such as nanosheets, nanowalls and nanojunctions/networks are important components for nanoscale devices with various applications due to their large surface areas that can be exposed to gaseous environments [20–23]. Therefore, it will be very promising to synthesize 2D NiO nanostructures.

In this study, the authors present a simple approach to realize 2D NiO nanowalls by thermal treatment of a Ni thin film deposited onto a stainless steel substrate. The experimental processes are first described. The as-synthesized NiO nanowalls are then characterized by scanning electron microscopy (SEM), energy-dispersive x-ray analysis (EDX), x-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM).

2. Experiment

A 1 μm thick Ni thin film is deposited onto a stainless steel substrate (AISI 321) by sputtering under a vacuum level of

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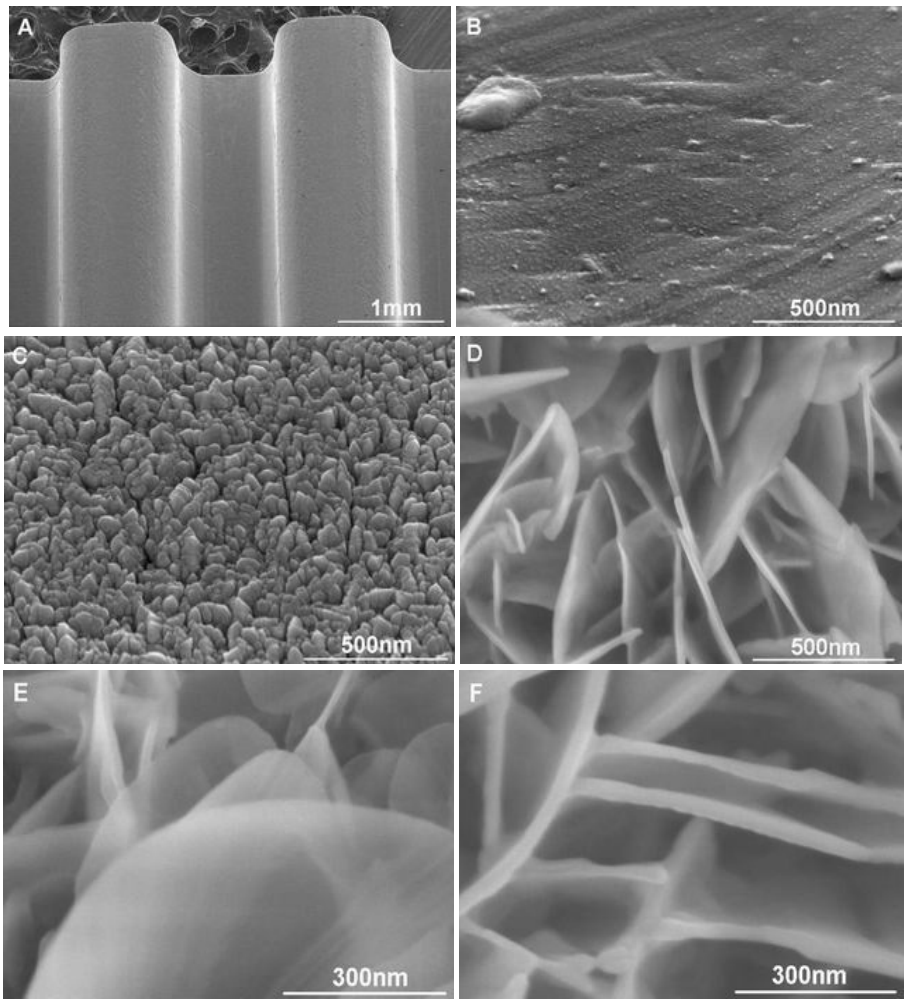

Figure 1. SEM images of: (A) stainless steel substrate, (B) enlarged view of the substrate, (C) as-deposited Ni film, (D)–(F) annealed Ni film at 600 °C for 4 h.

4×10^{-4} mbar and the substrate temperature is about 50 °C during the deposition. The composition of the stainless steel substrate is Fe (73%), Cr (17.3%), Ni (9.1%), Ti (0.55%), C (0.04%) and N (0.01%). The substrate with the Ni thin film is then cut into small chips (2.5 cm × 2.5 cm). After being blow-cleaned by N_2, the chips are placed onto a clean silicon wafer that is put onto a quartz boat. The quartz boat is positioned into a quartz tube (100 cm in length, 17 cm in diameter) that is mounted inside a horizontal tube furnace. A flow of high-purity N_2 is first introduced into the quartz tube at a flow rate of 2000 sccm for 20 min to remove air in the system, and then adjusted to 400 sccm accompanied by an O_2 flow at a rate of 100 sccm. The furnace is heated to the set-point temperatures with a heating rate of about 18 °C min^{-1} at around 1 atm. After being held for the desired time, the furnace is cooled down naturally to room temperature. The as-realized NiO nanowalls on the stainless steel substrate are directly characterized by SEM and XRD. Normal XRD patterns are recorded on a Bruker D4-Endeavor diffractometer using Cu Kα radiation (40 kV, 40 mA) from 20° to 100° in 2θ with a 0.016° step scan, a real time/step of 0.13 s on a linear Bruker LynxEye detector and 30 rotation min^{-1}. Grazing XRD measurements are made on a D5000 Bruker diffractometer with Cu Kα radiation using a grazing (1° maximum angle) incidence geometry over 35° to 65° in 2θ (step size is 0.03° and 35 s/step). For TEM and HRTEM observations, nanowalls are manually scratched from the stainless steel substrate, mixed with ethanol and deposited onto carbon-coated copper girds. TEM images and electron diffraction patterns are obtained on a JEOL 2010 microscope running at 200 kV. HRTEM images are taken with a JEOL 2100F microscope operating at 200 kV.

3. Results

3.1. SEM characterization

Figure 1(A) shows a SEM image of the stainless steel substrate used for the process. The substrate is fabricated to have a larger surface area than a flat substrate. The enlarged view of the substrate surface is shown in figure 1(B). Figure 1(C) is the substrate surface after depositing a 1 μm thick Ni thin film by sputtering. The average diameter of the Ni particles on the surface is about 20–50 nm. After annealing the Ni film at 600 °C for 4 h, NiO nanowalls grow from the film surface as shown in figure 1(D). Figure 1(E) is a side view of the

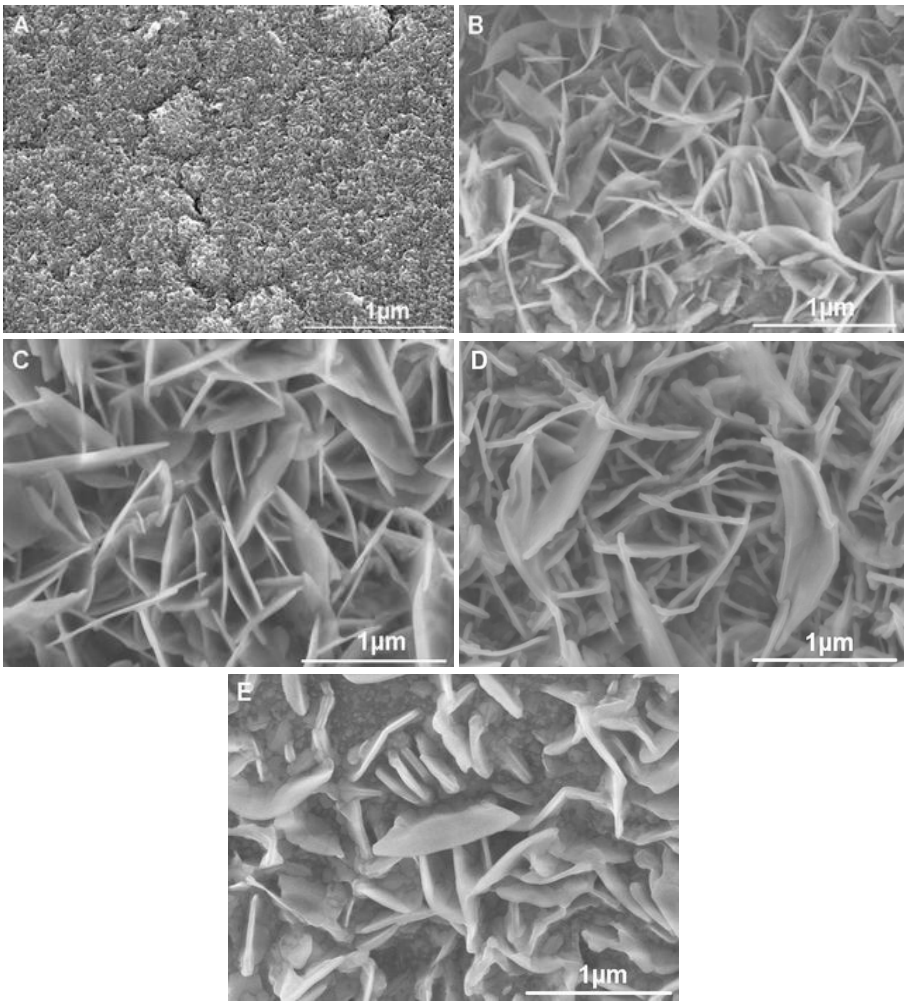

Figure 2. SEM images of the Ni film annealed for 4 h at different temperatures: (A) 400 °C, (B) 500 °C, (C) 600 °C, (D) 650 °C and (E) 700 °C.

nanowalls. Some of them are transparent, which suggests very thin walls. A top view of the nanowalls is shown in figure 1(F). The average thickness of the nanowalls is around 20–40 nm and most of them grow perpendicularly along the film surface.

Figures 2(A)–(E) show the SEM images of the annealed Ni thin film for 4 h at 400, 500, 600, 650 and 700 °C, respectively. After annealing at 400 °C, very tiny wall-like structures are formed on the surface of the film. When the annealing temperature is increased to 500 °C, nanowalls start to grow from the surface. After the annealing temperature is further increased to 600 °C, the as-grown nanowalls become larger, denser and more uniform. However, when the annealing temperature is too high (700 °C), only sparse and thick nanowalls are formed on the film surface. It proves that the annealing temperature has a great effect on the growth of the nanowalls.

To further understand the formation of the NiO nanowalls, SEM images of the annealed Ni thin film at 600 °C for different times are taken and shown in figures 3(A)–(F). After annealing for 1 min, very tiny nanowalls start to grow out of the thin film. For such a small time annealing, the furnace is first heated to 600 °C with a heating time of about 33 min. After being held for 1 min, the furnace is cooled down naturally to room temperature. After 5 min, the nanowalls become longer and higher. After 20 min, the length and height of the nanowalls are further increased. After annealing for 1 h, the nanowalls are well formed as compared to those in figure 1(D) that are annealed for 4 h. However, according to the cross-sectional views as shown in figures 3(E) and (F), the nanowalls after annealing for 4 h are much higher than those synthesized with an annealing time of 1 h.

Vapor–liquid–solid (VLS) and vapor–solid (VS) mechanisms have most commonly been used to account for the growth of nanostructures [24, 25]. On the basis of our SEM observations, the VLS mechanism could be excluded because we do not observe terminators on the nanowalls. The VS mechanism may also be ruled out for several reasons. First, the growth temperatures are much lower than the boiling point of bulk Ni (2913 °C). Second, all of the nanowalls are observed to grow out of the Ni thin film and nowhere else do we find any trace of nanowalls. Third, the annealing gas flow rate is increased to 10 000/2500 (N_2/O_2) sccm to ensure there is not much vapor staying near the sample surface during the annealing. This flow rate is much larger than those usually employed

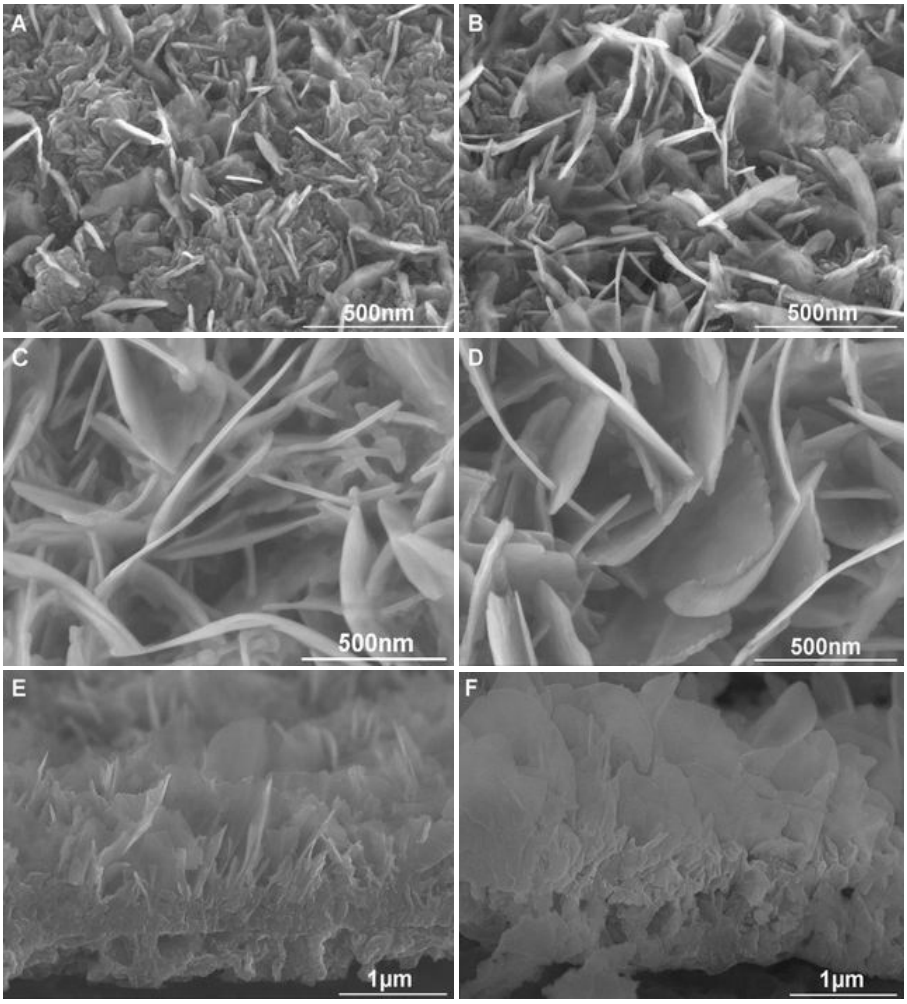

Figure 3. SEM images of the Ni film annealed at 600 °C for different times: (A) 1 min, (B) 5 min, (C) 20 min, (D) 1 h, (E) 1 h, cross-section and (F) 4 h, cross-section.

for growth of the nanostructures [26, 27]. The morphology of the as-prepared nanowalls is similar to that synthesized with a gas flow rate of 100/25 (N_2/O_2) sccm. This suggests that vapor does not play an important role in the growth of the nanowalls.

Consequently, we believe that the growth mechanism is based on the diffusion of the Ni species from the base Ni film. Internal diffusion is unlikely because it usually requires higher activation energy than surface diffusion. Moreover, as increasing the reaction time at constant temperature does not increase the thickness of the nanowalls but only their length (figure 3), we believe that the nanowalls grow at the top by surface diffusion of Ni^{2+} ions from base to top. The effect of annealing temperature on the growth of the nanowalls shown in figures 2(A)–(E) can be explained as follows. When the temperature is too low (<450 °C), although surface oxidation does occur, the Ni^{2+} surface diffusion rate is low and only very small nanowalls are formed after 4 h. In the range 500–650 °C, the increased diffusion rate of Ni^{2+} enhances the growth of the nanowalls and they uniformly cover the substrate surface. However, when the annealing temperature is too high (>650 °C), the very thin nanowalls will collapse to reduce the surface energy and there are fewer but thicker nanowalls formed.

3.2. EDX/XRD characterization

The elements of the as-deposited Ni film before and after annealing are identified by EDX as shown in figures 4 and 5, respectively. To remove the effect of the stainless steel substrate, the thin films are manually scratched from the substrate and deposited on a clean silicon chip for EDX characterization. The main elements seen in the EDX spectrum are Ni and Si for the as-deposited Ni film, where Si comes from the silicon chip. After annealing under a N_2/O_2 gas flow at 600 °C for 4 h, O is clearly seen from the EDX spectrum due to the oxidation of Ni.

The deposited Ni films before and after annealing are also characterized by XRD. Figure 6 shows the XRD pattern of the as-deposited Ni film on the stainless steel substrate. Figure 7 is the XRD pattern of the film after annealing at 600 °C for 1 h. Both Ni and NiO diffraction lines appear in the pattern. The as-deposited Ni film is partially oxidized into NiO. After annealing at 600 °C for 4 h, only NiO and the

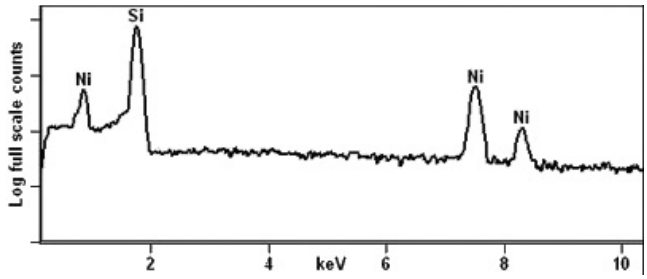

Figure 4. EDX spectrum of the as-deposited Ni film.

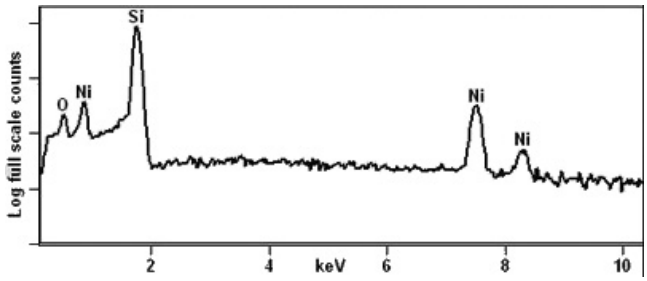

Figure 5. EDX spectrum of the Ni film after annealing at 600 °C for 4 h.

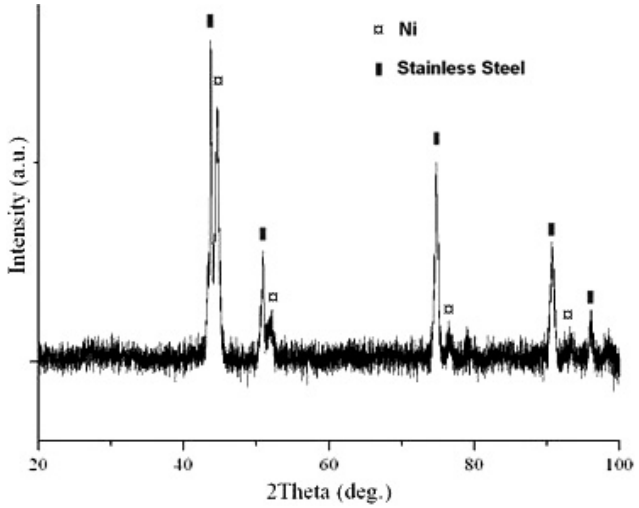

Figure 6. XRD pattern of the as-deposited Ni film.

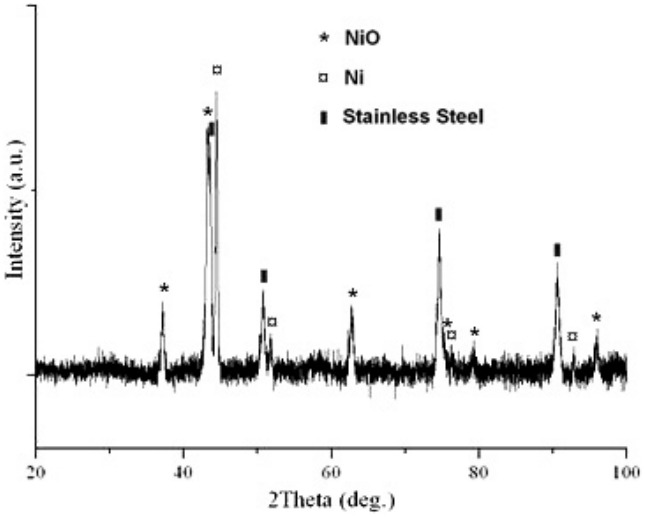

Figure 7. XRD pattern of the Ni film after annealing at 600 °C for 1 h.

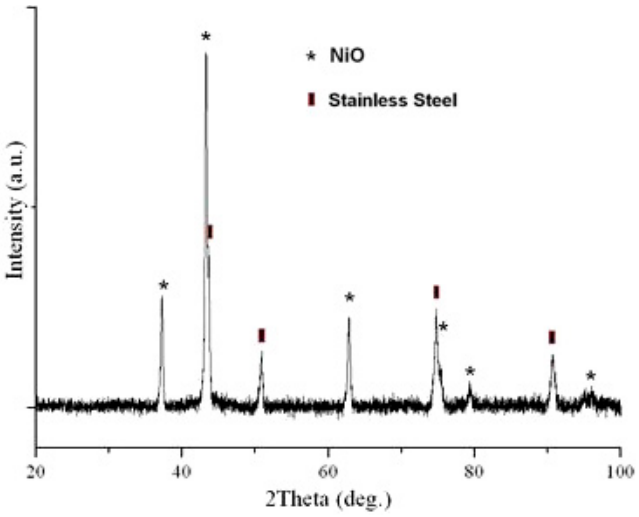

Figure 8. XRD pattern of the Ni film after annealing at 600 °C for 4 h.

substrate diffraction lines can be seen from the XRD pattern as shown in figures 8 and 9. This means that Ni film is converted into NiO nanowalls and NiO film under the nanowalls (see also figures 3(E) and (F)). Therefore, XRD results indicate that the NiO/Ni ratio in the nanowall film increases with annealing time until the entire Ni film is oxidized into pure NiO.

3.3. TEM/HRTEM characterization

Figure 10 shows the TEM image of the NiO nanowalls and an electron diffraction pattern of the arrowed nanowall indicating a single-crystal structure. It is a view of the (111) reciprocal lattice plane of NiO. Figure 11 is a HRTEM image of the nanowalls. There are two slices of the nanowalls inside the image. The lower larger slice is not flat. That is why its lattice fringes are not continuous. The upper slice is overlapped onto the lower one. But the lattice fringes of the covered part of the lower slice can still be seen, which is due to the transparent property of the very thin nanowall. The interplanar spacing for both slices is about 0.24 nm, which corresponds to the (111) plane of cubic crystalline NiO, indicating that the growth plane on the nanowalls is along the [111] direction. Based on the TEM/HRTEM observations, the NiO nanowalls are single-crystal.

4. Conclusion

Two-dimensional NiO nanowalls have been synthesized by thermal treatment of a Ni thin film deposited by sputtering onto a stainless steel substrate under a N_2/O_2 gas flow. The thermal treatment temperature has a significant effect on the

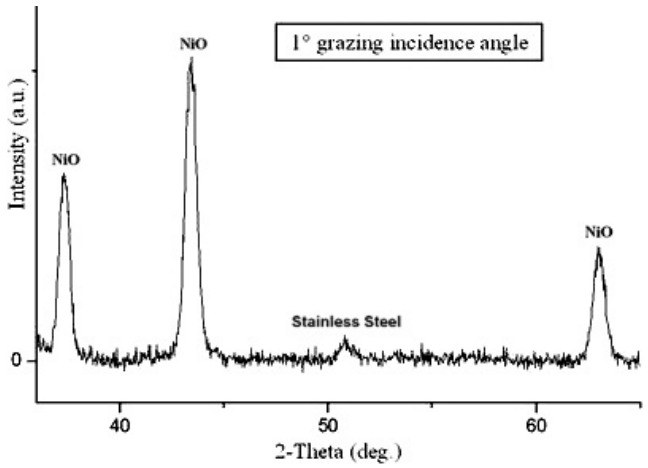

Figure 9. Grazing XRD pattern of the Ni film after annealing at 600 °C for 4 h.

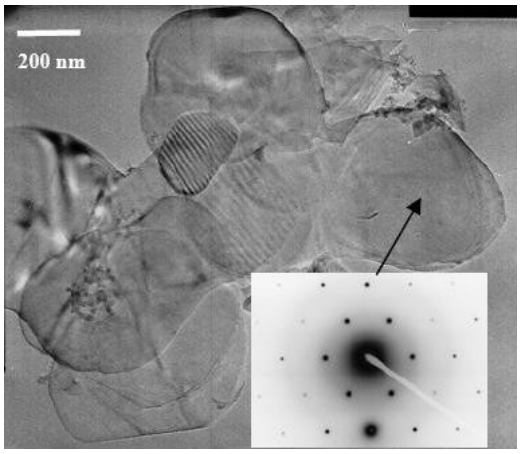

Figure 10. TEM image and ED pattern of the nanowalls annealed at 600 °C for 4 h.

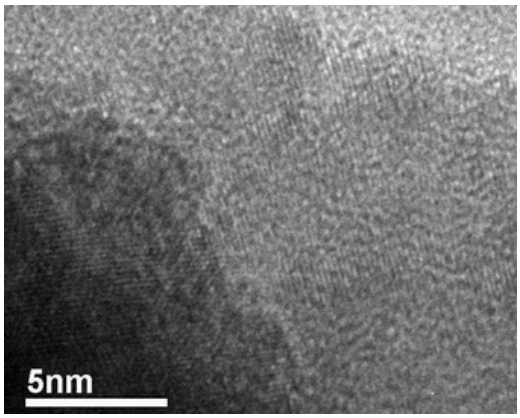

Figure 11. HRTEM image of the nanowalls annealed at 600 °C for 4 h.

morphology of the nanowalls. Large-area, dense and uniform nanowalls can only be formed within a narrow temperature range from 500 to 650 °C. The size of the nanowalls and the NiO/Ni ratio of the nanowall film increase with the thermal treatment duration time. After annealing at 600 °C for 4 h, the Ni film is converted into NiO nanowalls and NiO film under the nanowalls. TEM/HRTEM results show that the NiO nanowalls are single-crystal. The surface diffusion of Ni^{2+} ions from the Ni base film is believed to be a key factor for the growth of the NiO nanowalls.

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