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NiO Nanostructured Honeycomb Realized by Annealing Ni Film Deposited on Silicon

Kaili Zhang^{1,*}, Carole Rossi^{1,*}, Pierre Alphonse², and Christophe Tenailleau²

¹LAAS-CNRS, Université de Toulouse, 7 av du colonel Roche, 31077 Toulouse Cedex 4, France

²CIRIMAT, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 9, France

Two-dimensional nanostructures have various interesting applications due to their large surface areas. In this study, we propose a simple approach to synthesize two-dimensional NiO nano honeycomb by thermal annealing of Ni thin film deposited onto silicon substrate by thermal evaporation. The effects on the nano honeycomb morphology of the annealing temperature and time are investigated. Because the NiO nano honeycomb is realized onto silicon substrate, a basic material for microelectronics and micro-system, this will probably open the door to integrate the nano honeycomb into micro-system, thus leading to nano based functional devices. The as-synthesized NiO nano honeycomb is characterized by SEM, XRD, and surface area measurement.

Keywords: Nano NiO Honeycomb, Annealing, Ni Thin Film, Silicon Substrate, Surface Area.

1. INTRODUCTION

Nano metal oxides have received steadily growing attention because of their fascinating properties and various applications compared to their bulk or micro counterparts.¹ Among the transition metal oxides, NiO has attracted intensive interests due to its applications in diverse fields, including thermal electric device,² gas sensor,³ conducting electrodes,⁴ electrochromic films,⁵ and catalysis.⁶⁻⁸ Up to now, a variety of methods have been employed to realize nanostructured NiO. NiO nanoparticles have been synthesized through organic solvent method,⁹ water-in-oil microemulsion,¹⁰ and thermal decomposition of NiC₂O₄ precursor.¹¹ One-dimensional (1D) NiO nanowires, nanorods, and nanotubes have been fabricated by wet chemical route,¹² electrochemical deposition based on anodic alumina membranes,¹³ thermal decomposition of NiC₂O₄ precursor,¹⁴ oxidation of NiS,¹⁵ thermal decomposition of the precursor deposited in NiSO₄ aqueous solution with urea,¹⁶ sol-gel method,¹⁷ thermal oxidation of a thin nickel foil,¹⁸ and template synthesis technique.¹⁹ Besides NiO nanoparticles and 1D NiO nanostructures, it will be interesting to realize two-dimensional (2D) NiO nanostructures. It is known that 2D nanostructures such as nanowalls,^{20,21} nanojunctions,²² and nanosheets²³ are important components for nanoscale devices with various applications because of their large

surface areas that can be exposed to gaseous environments. However, no approach is reported in the literature to realize 2D NiO nanostructures. Moreover, 2D nanostructures are often claimed to have large surface areas. Nevertheless, there are very few studies in the literature to quantitatively determine the surface areas of these 2D nanostructures.

In this study, we propose a very simple approach to synthesize 2D NiO nano honeycomb by thermal annealing of Ni thin film deposited onto silicon substrate. The nano honeycomb might have lots of potential applications due to its porous structure. Furthermore, the surface area of the 2D NiO nano honeycomb is quantitatively determined by gas adsorption measurement. By creating NiO nano honeycomb, the substrate surface area is substantially increased.

2. EXPERIMENTAL DETAILS

A 0.4 μm thick Ni thin film is deposited onto a 4-inch silicon substrate by thermal evaporation under a vacuum level of 7×10^{-6} mbar and the substrate temperature is about 45 °C during the deposition. The silicon substrate with Ni thin film is then cut into small chips. After being blow-cleaned by N₂, 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.

* Authors to whom correspondence should be addressed.

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 (400 °C, 500 °C, and 600 °C). After being held for the desired time, the furnace is cooled down to room temperature. The as-realized NiO nano honeycombs on silicon substrate are directly characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

The as-prepared NiO nano honeycombs are also characterized by surface area measurement. Ni with a thickness of 0.4 μm is deposited onto both sides of a double polished 4-inch silicon wafer (thickness: 422 μm). The wafer is then cut into four chips with similar weights. Three of the chips are annealed for 6 h under a N_2/O_2 gas flow at 400 °C, 500 °C, and 600 °C, respectively. After annealing, the three chips are cut into pieces small enough to enter an analysis cell used for the surface measurement. The Krypton adsorption isotherms are determined at 77 K, by volumetric method, with a Micromeritics ASAP 2010 M. The isotherms are recorded in the relative pressure range from 0.06 to 0.35. The samples are outgassed under primary vacuum at 300 °C for 4 h. The surface area is computed from isotherm using the B.E.T. method.²⁴

3. RESULTS

3.1. SEM Characterization

Figure 1(A) is a 30° tilted view SEM image of the deposited 0.4 μm thick Ni thin film onto silicon substrate by thermal evaporation. The diameter of the deposited Ni particles on the film surface is about 10–30 nm. Figures 1(B–D) show the 30° tilted view SEM images of the annealed Ni thin film for 6 h at 400 °C, 500 °C, and 600 °C, respectively. The surface morphology is considerably changed after the thermal annealing. After annealing at 400 °C, NiO nano honeycomb is formed. But it seems that the annealing temperature is too low to convert the thin film into uniform nano honeycomb. When the thin film is annealed at 500 °C, uniform nano honeycomb is formed with a wall thickness of 50–100 nm. Experiments also show that uniform nano honeycomb can be created on the entire surface of a 4-inch silicon wafer. Therefore, it is suitable for mass production. After annealing at 600 °C, the wall thickness of the created honeycomb becomes thicker due to the sintering of nanocrystals and the honeycomb structure starts to collapse.

Figures 2(A–D) show the 30° tilted view SEM images of the annealed Ni thin film at 500 °C for 30 s, 1 min, 20 min, and 1 h, respectively. After annealing for 30 s,

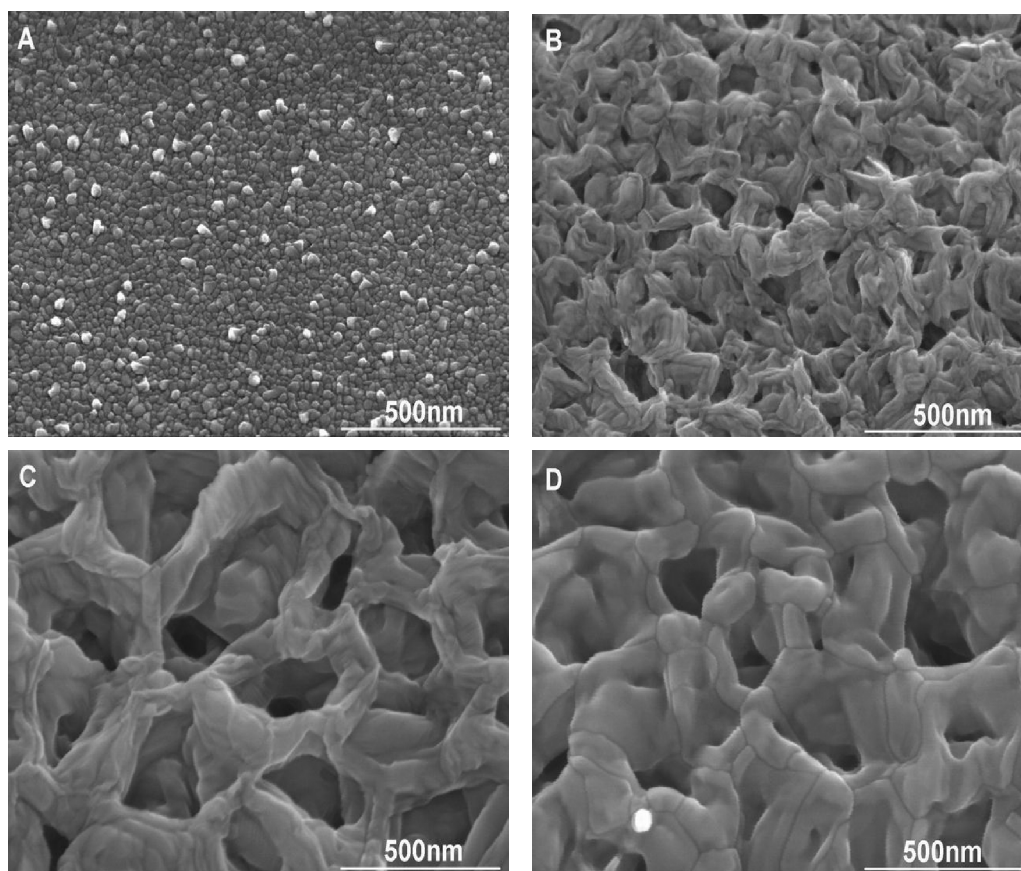


Fig. 1. 30° tilted view SEM images of: (A) Ni thin film, (B)-(C)-(D) annealed Ni film for 6 h at 400 °C-500 °C-600 °C, respectively.

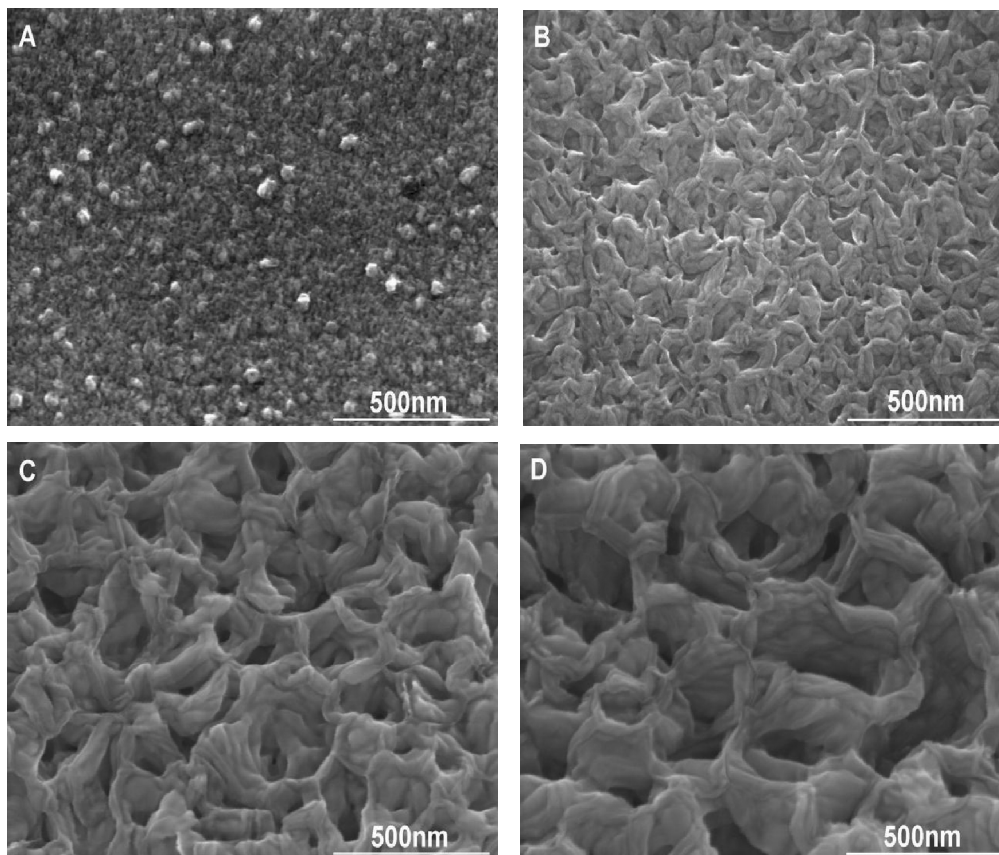


Fig. 2. 30° tilted view SEM images of annealed Ni film at 500 °C for different times: (A) 30 s, (B) 1 min, (C) 20 min, and (D) 1 h.

very tiny pits start to appear on the Ni thin film surface. Nano honeycomb is formed on the top shallow surface of the thin film after heating for 5 min. After annealing for 20 min, the size of the nano honeycomb becomes larger. When the annealing time is more than 1 h, uniform nano honeycomb is formed as shown in Figure 2(D) (1 h) and Figure 1(C) (6 h).

To further understand the formation of the NiO nano honeycomb and the oxidation of the Ni thin film, cross-section view SEM images of annealed Ni film at 500 °C for different times are taken and shown in Figures 3(A–D). After annealing for 1 min, the NiO nano honeycomb is only formed at the top shallow surface of the thin film. Most of the thin film remains to be Ni. After 20 min, about half of the thin film becomes porous. When the annealing time is 1 h, most of the thin film is oxidized into nano honeycomb and some of the nano holes extend through the entire thickness of the thin film. After heating for 6 h, the entire Ni thin film is oxidized into porous NiO. The resulting film thickness is increased by more than two times due to the created porosity.

3.2. XRD Characterization

The structure of the as-synthesized nano honeycomb after annealing at 500 °C for 20 min and 6 h is characterized by XRD as shown in Figures 4 and 5, respectively. After

annealing for 20 min, both Ni and NiO are present. After annealing for 6 h, only NiO diffraction lines can be seen from the XRD pattern, thus the Ni thin film has been totally transformed into NiO. Therefore, XRD results confirm that the NiO/Ni ratio in the thin film increases with the annealing time until the entire Ni thin film is oxidized into pure NiO. It is believed that at temperatures above 200 °C, Ni normally reacts with silicon to form nickel silicide. However, no nickel silicide is observed at various annealing stages in our experiments. Before Ni film deposition, the natural silicon dioxide thin layer on the silicon wafer surface was not removed. We believe that it is the silicon dioxide layer that prevents the formation of nickel silicide.

3.3. Surface Area Characterization

The change in surface area according to the annealing temperature is shown in Figure 6. Compared to silicon surface area, after annealing for 6 h at 400 °C, 500 °C, and 600 °C, the surface area is increased by about 5, 12, and 8 times, respectively.

3.4. Application Example

The synthesized uniform 2D NiO nano honeycomb is supposed to have applications in thermal electric device, gas

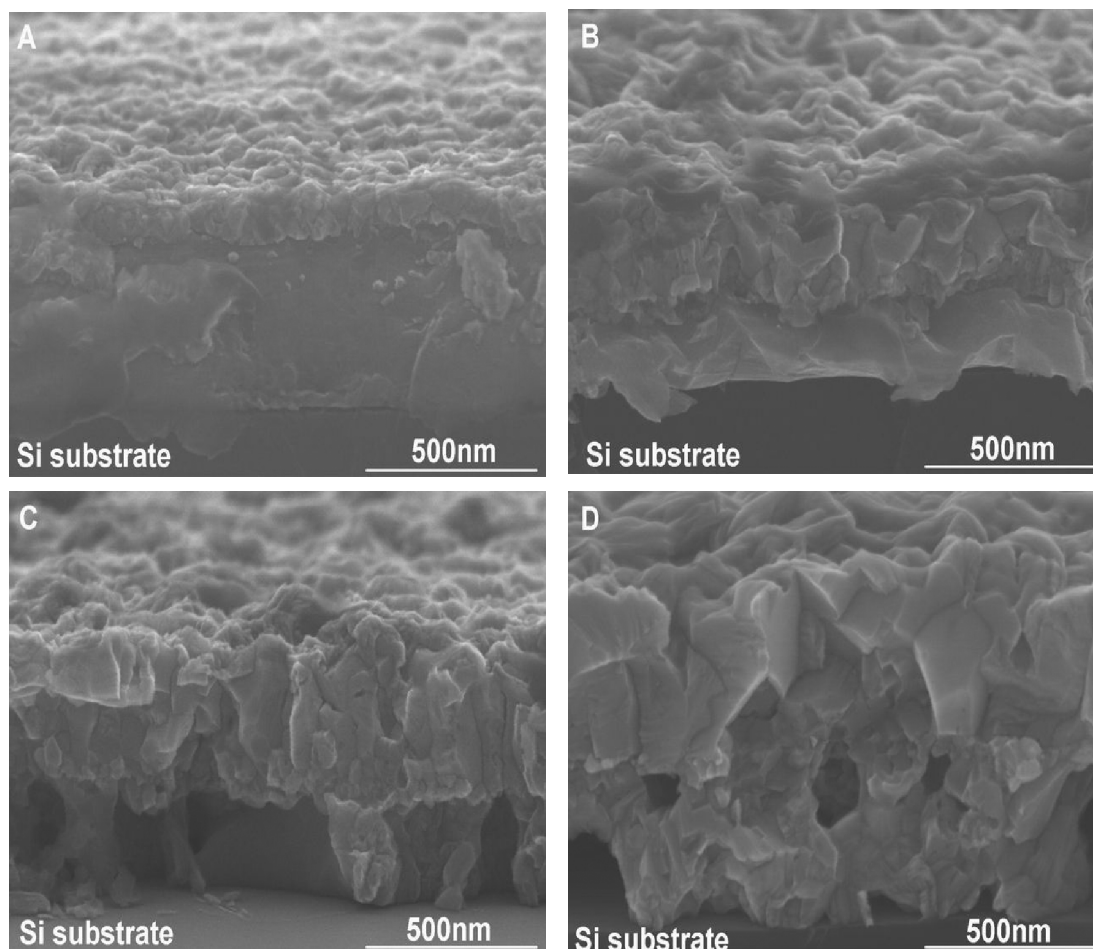


Fig. 3. 3 Cross-section view SEM images of annealed Ni film at 500 °C for different times: (A) 1 min, (B) 20 min, (C) 1 h, and (D) 6 h.

sensor, conducting electrodes, and catalysis. Another interesting application is to realize NiO/Al based nano energetic material as suggested in Ref. [25]. Figure 7 shows the NiO nano honeycomb after Al integration. By comparison

with Figure 1(C) it can be seen that Al is intimately integrated with NiO nano honeycomb. This is expected to result in faster energy release rate caused by the enhanced interfacial contact area. Most interestingly, the NiO nano

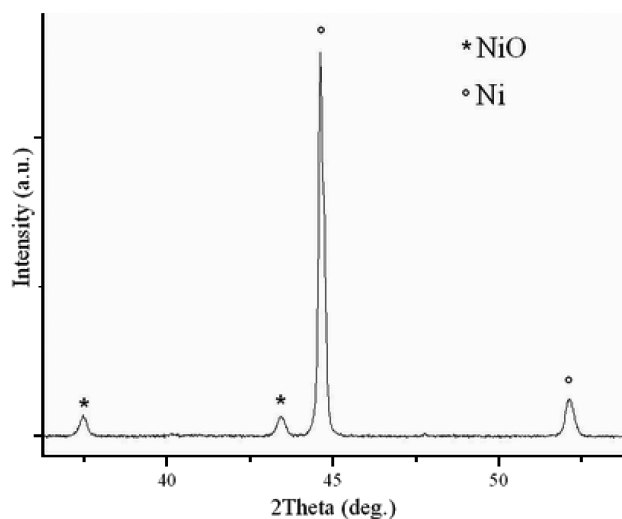


Fig. 4. XRD pattern of the Ni film after annealing at 500 °C for 20 min.

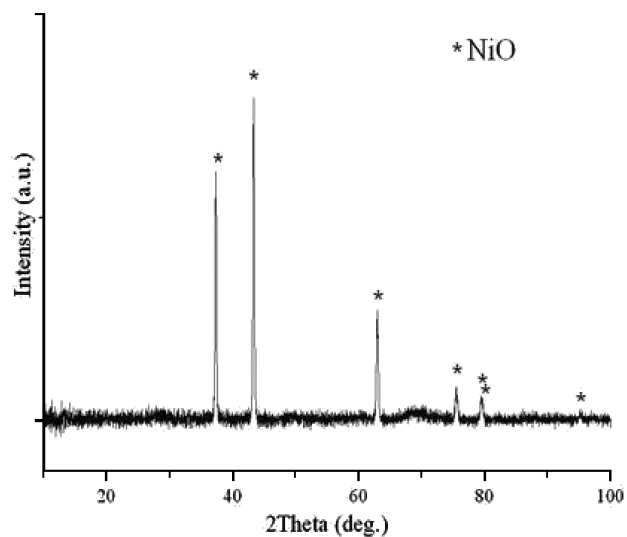


Fig. 5. XRD pattern of the Ni film after annealing at 500 °C for 6 h.

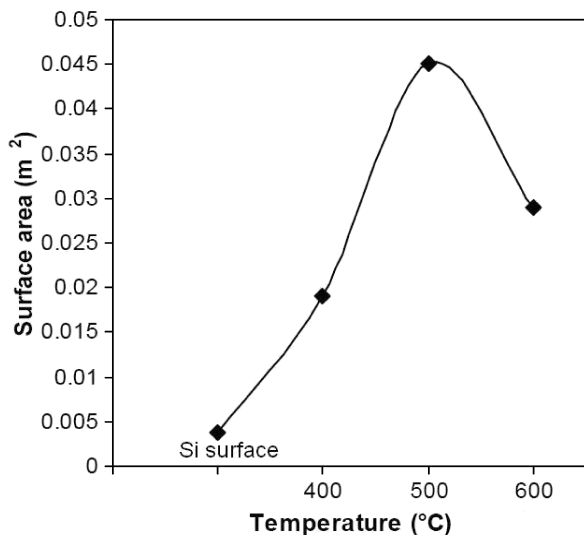


Fig. 6. Surface area variation with annealing temperature.

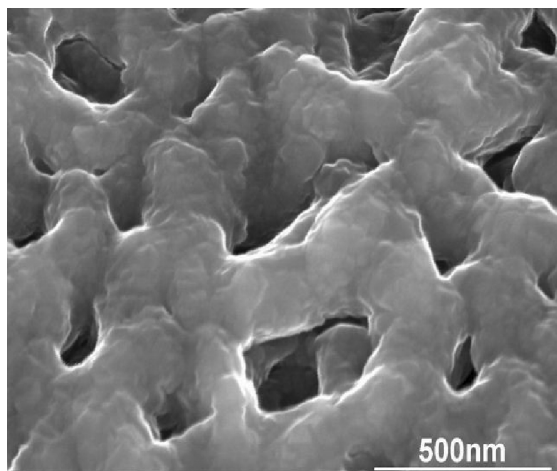


Fig. 7. NiO nano honeycomb after Al integration.

honeycomb is realized onto silicon, a basic material for microelectronics and micro-system. Therefore, this will probably open the door to integrate the nano honeycomb into micro-system, thus leading to nano based functional devices.

4. CONCLUSION

Two-dimensional NiO nano honeycomb has been realized by thermal annealing of Ni thin film deposited onto silicon substrate by thermal evaporation under a N_2/O_2 gas flow. It is found that the annealing temperature has a great effect on the morphology of the nano honeycomb. Uniform nano honeycomb can only be formed at an annealing temperature of 500 °C. The nano honeycomb size, NiO/Ni ratio and porosity of the thin film increase with the annealing time. After annealing at 500 °C for 6 h, the Ni thin film

is converted into pure porous NiO and the surface area is increased by about 12 times due to the formation of NiO nano honeycomb on the substrate surface. Since the 2D NiO nano honeycomb is synthesized onto silicon substrate that is a basic material for microelectronics and micro-system, it will be easier to integrate the nano honeycomb into micro-system, thus leading to nano based functional structures.

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