

Research Paper

Effect of Surface Treatment on the Formation of NiO Nanomaterials by Thermal Oxidation

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Abstract Thermal oxidation has significant potential for use in synthesizing metal-oxide nanostructures from metallic materials. However, this method has limited applicability to the synthesis of multi-morphology NiO from Ni foil. Techniques consisting of mechanical and chemical approaches were used to pre-treat the Ni foil (prior to oxidation) to promote the formation of nanowires and nanoplates on the NiO layer. These morphologies were realized on the Ni foils scratched by sand paper and a knife, respectively, and subsequently heat-treated at 500°C for 24 h. Small nanowires (diameter: <10 nm) formed on the Ni foil treated by absolute HNO₃ and then oxidized at 500°C for 24 h. The formation of various morphologies (on the pre-treated Ni foil), which differ from that formed in the case of pristine Ni foil after oxidation, may be attributed to the surface melting phenomenon that occurs during the nucleation process.

Keywords: NiO, Thermal oxidation, Surface treatment, Nanowires, Nanoplates

I. Introduction

In recent years, nanomaterials have received significant attention from scientists and industry, owing to their excellent electronic, optical, mechanical, and thermal properties, which are superior to those of bulk materials. The metal-oxide semiconductor is the most important and well-studied candidate for nanomaterials. To date, many techniques and methods have been developed to synthesize metal-oxide nanostructures via bottom-up and top-down approaches. These approaches include, thermal evaporation [1], sputtering [2], thermal oxidation [3], vapor-liquid-solid (VLS) or vapor-solid (VS) processes [4,5], hydrothermal methods [6], and solution methods [7]. Among these methods, thermal oxidation of metallic foils is considered a cost-effective method for growing metal-oxide nanostructures, through direct oxidization of the metals in the environment. By using this simple method, nanostructured oxides of Cu [8], Co [9], Fe [10], Ge [11], Zn [12], and Ni [13] have been successfully synthesized in the form of nanorods, nanowires, and nanoplates.

The transition metal oxide, NiO, has a stable wide band gap of 3.6-4.0 eV and hence, has been used in various applications, such as gas sensors [14], conducting electrodes [13], solar cells [15], and catalysts [16]. Synthesis of NiO nanostructures, via thermal oxidation of Ni foil, is more difficult than that of other oxides such as CuO, CoO, ZnO

or Fe₂O₃. However, plasma-assisted (radio frequency of 200 W) direct growth of NiO nanowalls on Ni foils, can be achieved at 700°C/1500 mTorr [13]. NiO nanowires may also be grown, via thermal oxidation, by conducting a surface treatment in a chemical solution prior to heating [17]. The main idea of this technique is to prepare seeds on the foil surface, in order to promote growth at the seed locations during the heat treatment. In this study, the growth process of NiO on Ni foils, subjected to mechanical scratching (by sand paper and knife) and chemical etching (in HNO₃), was investigated. By using this technique, NiO nanowires and nanoplates were fabricated at 500°C, directly on the surface of the Ni foil. This simple technique can be used to enhance the synthesis of metal-oxide nanostructures, achieved via the thermal oxidation method.

II. Experimental

Figure 1 shows a schematic of the experimental procedure. First, Ni foil was divided into 10×10 mm² pieces. The surface of each piece was subjected to three respective treatments: scratching by a knife, scratching by sand paper, and soaking for 5-15 min in 20 mL of an aqueous solution of 100% HNO₃. Afterwards, the foils were sonicated in deionized water and alcohol for 10 min. The pristine Ni foils were placed in an alumina boat, fixed at the center of a horizontal furnace, and heated at 400-800°C for 24 h; the temperature was increased at a rate of 5°C/min. During the treatment, a mixture gas of oxygen and nitrogen (with a ratio of R(O₂:N₂)=1:5) is introduced

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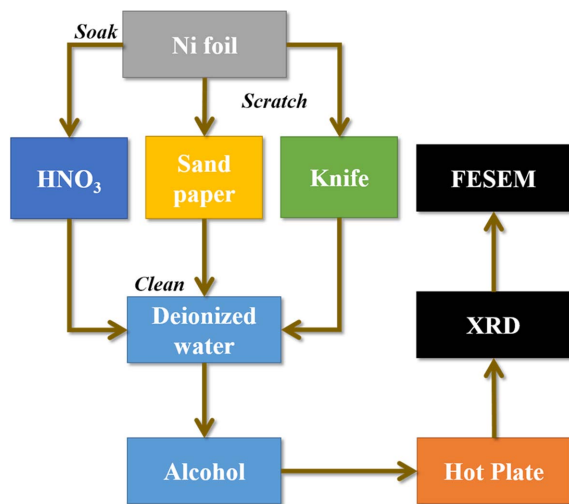


Figure 1. Experimental process.

into the tube at a flux rate of 30 sccm. After the treatment, the samples are cooled naturally. The surface-treated samples were then annealed at 500°C for 24 h.

The surface morphology of all the samples was characterized via field-emission scanning electron microscopy (FE-SEM; JSM-6701F). In addition, X-ray diffraction (XRD, XPERT-PRO) analysis of the samples was performed at a potential and current of 40 kV and 30 mA, respectively, using Cu-K α radiation ($\lambda=1.54178 \text{ \AA}$).

III. Results and Discussion

The series of peaks at 37.3°, 43.3°, 63.8°, 75.5°, and 79.4° in the XRD patterns (figure 2) of the pristine foils treated at 400-800°C correspond to NiO (111), NiO (200), NiO (220), NiO (311), and NiO (222) (JCPDS file No. 98-009-2132). The three major peaks at 44.6°, 52°, and 76.5° are attributed to Ni (111), Ni (200), and Ni (220) (JCPDS file No. 98-004-3397). Furthermore, the stronger NiO peaks suggest that, compared to the layer formed at lower

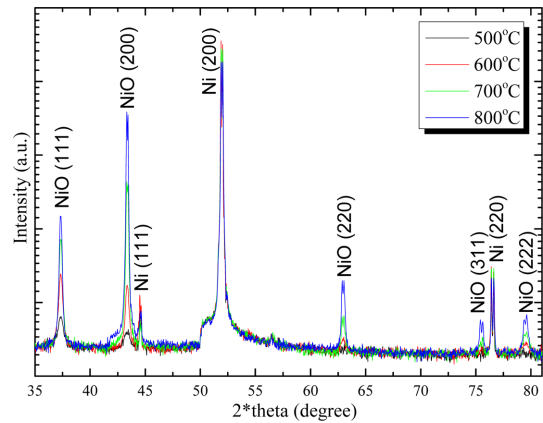


Figure 2. X-ray diffraction pattern of the pristine Ni foil treated at 400-800°C.

temperatures, a thicker and more crystalline oxide layer is formed on the Ni surface at higher treatment temperatures. The oxide layer constitutes the only contamination on the sample surface.

FE-SEM images (figure 3) of the pristine foil treated at 400-500°C show that the foil surfaces of both samples are composed of many small (~20-100-nm-sized) grains. At a temperature treatment of 400°C (figure 3a), the grains are predominantly spherical or rectangular, whereas the foil surface treated at 500°C (figure 3b), consists of many small plates. The grain size increases to 200 nm, at a treatment temperature of 600°C. The surface of samples treated at 700°C consists of crystal-like grains with sharp polygonal boundaries and grain boundaries with lengths ranging from 120 nm-500 nm. In addition, the, the grain boundary length increases continuously at a treatment temperature of 800°C, and the shapeless appearance of the boundary is indicative of significant boundary migration at this temperature. The grains on the surface had typical morphology, however, despite the migration and crystallization that occur on the foil surface during the heat-treatment.

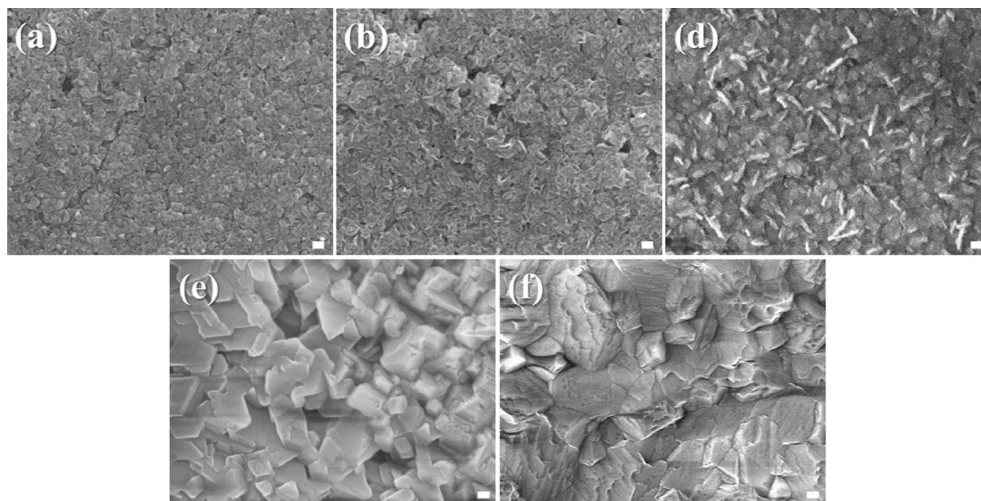


Figure 3. FE-SEM images of the pristine Ni foil surface treated at (a) 400°C, (b) 500°C, (c) 600°C, (d) 700°C, and (e) 800°C. The scale bar denotes 100 nm.

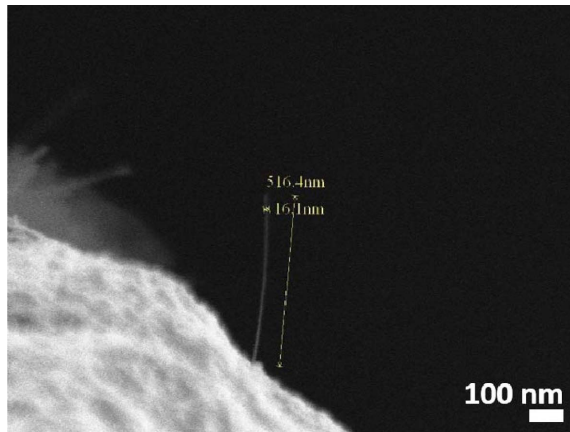


Figure 4. FE-SEM image of the side of the Ni foil treated at 500°C for 24 h.

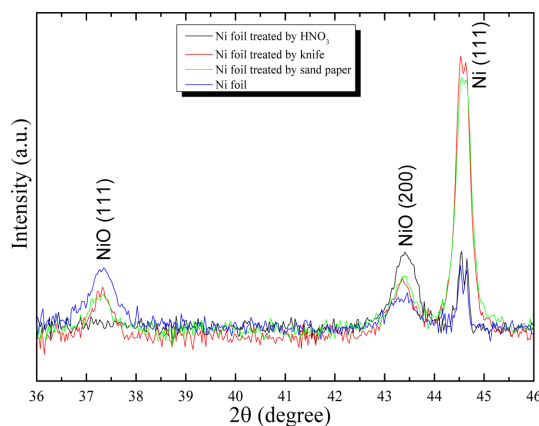


Figure 5. XRD patterns of the pre-treated (by HNO₃, knife, and sand paper) Ni foils, after a 24-h heat-treatment at 500°C.

Nanowires (~16 nm (diameter)×516 nm (length)) are partially formed on the cutting side of the Ni foil after a 24-h treatment at 500°C as shown in Fig. 4. This indicates that, for the same treatment conditions, the nucleation process may be enhanced by damage to the foil surface, which results in features (for example, nanowires) that have interesting morphology. Various types of seeds or nuclei

may be formed, depending on the surface treatment (mechanical or chemical) technique employed. Here, some of the Ni foil surfaces were scratched by a knife, others by sand paper, and the rest were etched with HNO₃; these surfaces were then all oxidized at 500°C, for 24 h.

The XRD patterns in figure 5 reveal details about the surface structure of the pre-treated Ni foils, which were subsequently oxidized at 500°C for 24 h. For example, in the case of the oxidized pristine foil, broader and weaker peaks occur at 37.4° and 43.4°, respectively, compared with those occurring in the patterns of other pre-treated samples; in contrast, the scratched samples give rise to sharp peaks, which have similar intensity. The sample pre-treated by HNO₃ gives rise to only one peak, i.e., a strong peak at 43.4°, which corresponds to the NiO (200). This suggests that the HNO₃-pre-treated sample consists of 1-D structures, such as nanowires or nanorods, whereas those scratched by the knife and sand paper consist of 2-D structures, such as nanoplates or nanowalls.

Figure 6 shows the FE-SEM images of the surface-treated samples, after 24 h of oxidation at 500°C. The surface of the sample scratched by sand paper (figure 6(a)) is composed of many grains, and is similar to that of the pristine Ni foil treated at 500°C. In addition, the sample surface consists of several coarse (~1-3-μm-sized) grains, and nanowires with an average diameter of 12 nm, are attached to the sides of these grains. The knife-scratched sample (figure 6(b)) has a high density of ~1-μm-sized (on average) nanoplates. However, many small (diameter: <10 nm) nanowires formed (at least partially) on the rough surface of the NiO layer present on the surface of the oxidized HNO₃-treated foil (figure 6(c-e)). It seems that the density of the nanowires on the Ni foil pre-treated in HNO₃ for 10 min is higher than that of the Ni foil pre-treated in HNO₃ for 5 min (figure 6(c, d)). As the Ni foil was pre-treated in HNO₃ for 15 min, less number of nanowires are found on the foil surface after thermal oxidation as in figure 6(e). This phenomenon suggests that the seeds or

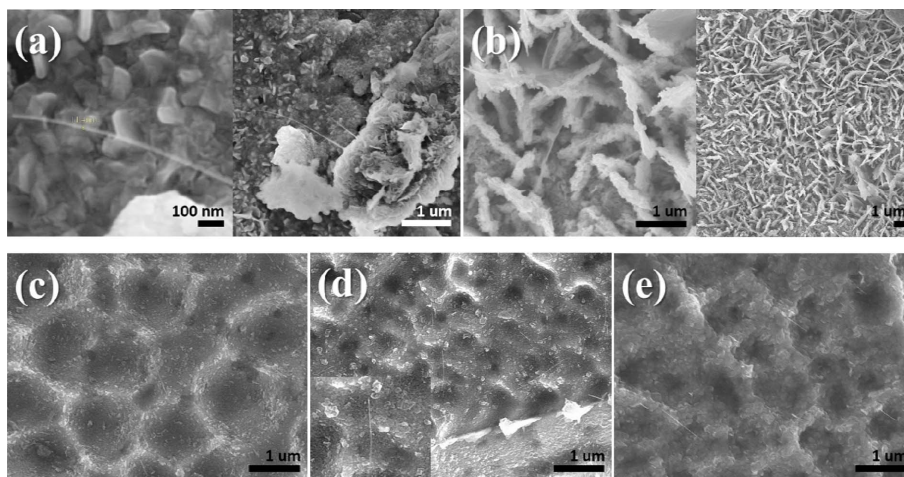


Figure 6. FE-SEM images of samples scratched by (a) sand paper, (b) knife, treated by HNO₃ for (c) 5 min, (d) 10 min, and (e) 15 min, after 24 h of oxidation at 500°C.

nuclei of nanowires may be formulated during the pre-treatment. Inversely, when the treatment time is too long, the as-created nuclei may be damaged or destroyed. At the moment, the optimum time we have found for pre-treating Ni foil in HNO₃ solution to growth the nanowires by thermal oxidation is 10 min.

The formation of complex structures on the surface of metallic foils during thermal oxidation has been attributed to growth mechanisms such as vapor-solid [18], solid-liquid-solid (SLS) [19], and stress-driven mechanisms [20]. All of those studies agree that the nucleation process constitutes the deciding factor in the final morphology of the oxide, after thermal oxidation. In recent work, we described the phenomenon of “surface melting” that occurs during the nucleation process of a Cu foil subjected to thermal oxidation [21]. Surface melting is initiated at surface defects, and results in the formation of a liquid-like layer at the oxide surface, even at temperatures significantly lower than the melting temperature of the oxide. Therefore, atoms and molecules on the surface melting layer can move and react with each other, leading to the formation of seeds and nuclei. This phenomenon depends strongly, however, on the oxidation of the host metal. Moreover, the oxide layers are more easily formed (at relatively lower temperatures) on the surfaces of metals such as Cu or Fe, than on Ni. Nucleation, via the surface melting phenomenon, occurs only at low temperatures. In fact, during high-temperature oxidation, nucleation may occur primarily through crystallization, but there is insufficient time for the formation of seeds or nuclei. The oxidation temperature of a metal is most easily reduced, by increasing the density of defects on the surface of the metal. This can be achieved via mechanical or chemical impact, such as scratching with sand paper or a knife, or etching with strong acids. Moreover, as shown in this study, different damaging techniques may yield different types of nuclei.

IV. Conclusions

Thermal oxidation of a pristine Ni foil was investigated at temperatures ranging from 500-800°C. Many small (~20-100-nm-sized) grains of NiO without nanowires were formed on the pristine Ni foil. However, nanowires (average diameter: 12 nm) and high-density nanoplates (plate size: 1-3 μm) were synthesized on the NiO surface by scratching the surface of the foil with sand paper and a knife, respectively. Small (diameter: <10 nm) nanowires grew on the foil that was pre-treated with HNO₃. In this experiment, the optimum treatment time in HNO₃ before thermal oxidation to grow nanowires is 10 min. The differing morphologies obtained, compared with that obtained in the case of the pristine Ni foil after thermal oxidation, are attributed to the surface melting phenomenon. In other words, at low temperatures (which are required for the nucleation process) surface defects lead to the formation

of the oxide layer and the surface melting layer. This surface pre-treatment technique has significant potential for the direct fabrication (via thermal oxidation) of multi-morphological oxide material, from any metal.

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