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# Integrating Al with NiO nano honeycomb to realize an energetic material on silicon substrate

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Kaili Zhang · Carole Rossi · Pierre Alphonse ·  
Christophe Tenailleau · Simon Cayez ·  
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**Abstract** Nano energetic materials offer improved performance in energy release, ignition, and mechanical properties compared to their bulk or micro counterparts. In this study, the authors propose an approach to synthesize an Al/NiO based nano energetic material which is fully compatible with a microsystem. A two-dimensional NiO nano honeycomb is first realized by thermal oxidation of a Ni thin film deposited onto a silicon substrate by thermal evaporation. Then the NiO nano honeycomb is integrated with an Al that is deposited by thermal evaporation to realize an Al/NiO based nano energetic material. This approach has several advantages over previous investigations, such as lower ignition temperature, enhanced interfacial contact area, reduced impurities and Al oxidation, tailored dimensions, and easier integration into a microsystem to realize functional devices. The synthesized Al/NiO based nano energetic material is characterized by scanning electron microscopy, X-ray diffraction, differential thermal analysis, and differential scanning calorimetry.

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## 1 Introduction

In recent years, researchers have found that energetic materials that are produced at the nanoscale have the promise of improved performance in various ways including energy release, ignition, and mechanical properties. At the nanoscale people can manipulate individual atoms and molecules and control their assembly into a large-scale bulk energetic material. The possibility exists to build large-scale energetic materials with a very high degree of uniformity, such as few/no defects, perfect crystalline structure, composites with molecularly engineered uniformity. Nano energetic materials (nEMs) represent a completely new frontier for energetic material research and development [1, 2]. Various ways have been used to realize nEMs such as physical mixing of nanopowders of fuel and oxidizer [3–5], sol-gel [6], aero-gel [7], and atomic layer deposition (ALD) [8]. Physical mixing presents some limitations, such as not homogeneous distribution of oxidizer and fuel, and poor compatibility with a microsystem. In sol-gel, the random distribution of the particles and the inherent organic impurities result in limited performance. An aero-gel and an ALD are not currently applicable for mass production. Blobaum et al. have deposited multilayer foils of oxidizer and fuel by sputtering [9]. This approach results in enhanced atomic mixing and reduced impurities. Porous-silicon-based nEMs were proposed in [10], which can be conveniently integrated into a silicon-based microsystem. Menon et al. realized Al/Fe<sub>2</sub>O<sub>3</sub> nEM by embedding an array of Fe<sub>2</sub>O<sub>3</sub> nanowires inside a thin Al film. This approach can control precisely the oxidizer and fuel dimensions [11]. Molecular self-assembly is also employed to prepare nEMs [12, 13], which could improve the homogeneity of the final material and control the fuel/oxidizer interfacial contact area. Recently, nano Al/CuO based nEM has been realized by inte-

grating nano Al with CuO nanowires grown from Cu film deposited onto silicon. This approach has the merits of enhanced contact, reduced impurities and Al oxidation, and easier integration into a microsystem [14].

In this study, nano Al/NiO nEM (also called nano thermite composite) is synthesized by integrating a nano Al with a two-dimensional NiO nano honeycomb realized onto a silicon substrate. This approach not only inherits the merits as in [14], but also has the advantage of low ignition temperature. The experimental processes are first presented. The fabricated Al/NiO nEM is then characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), differential thermal analysis (DTA), and differential scanning calorimetry (DSC).

## 2 Experiment details

The fabrication process starts with a 500- $\mu\text{m}$ -thick double-polished 4-inch p-type silicon substrate. The substrate is cleaned using acetone, chromic sulfuric acid mixture (RT2), thoroughly rinsed by deionized (DI) water and blow-dried by nitrogen. Then the substrate is placed into an oven at 200°C for 20 min for further drying. A 0.2- $\mu\text{m}$ -thick Ni thin film is deposited onto the silicon substrate by thermal evaporation in a thermal evaporator under a vacuum level of  $7 \times 10^{-6}$  mbar and the substrate temperature is being around 45°C during the deposition. The silicon substrate with Ni thin film is then placed onto a clean 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  $\text{N}_2$  is first introduced into the quartz tube at a flow rate of 2000 sccm for 20 min to remove the air

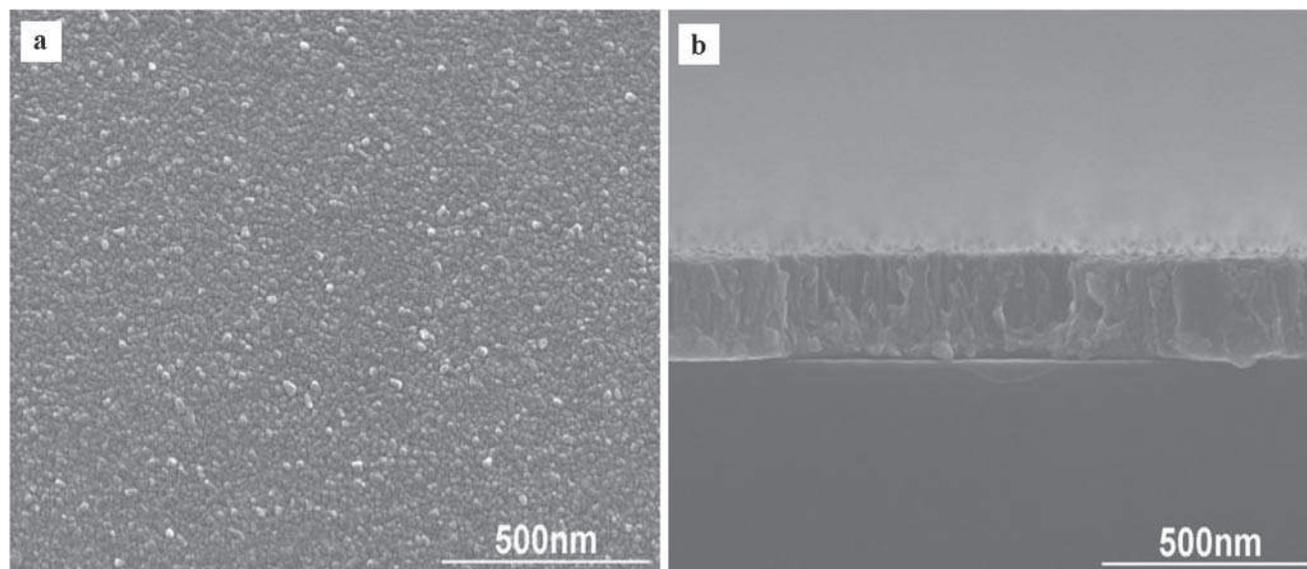
in the system, and then adjusted to 400 sccm accompanied by a  $\text{O}_2$  flow at a rate of 100 sccm. The furnace is heated from room temperature to 450°C. After being held at 450°C for 2 h, the furnace is cooled down naturally to room temperature. The silicon substrate with the oxidized Ni thin film is taken out of the furnace and put into a thermal evaporator. The Al is deposited by thermal evaporation onto the oxidized Ni thin film. The Al is deposited under a vacuum level of  $5 \times 10^{-6}$  mbar and the substrate temperature is being around 30°C during the deposition. The realized Al/NiO nEM on silicon substrate are directly characterized by SEM and XRD.

The heat of the reaction of the Al/NiO nEM is determined by DTA and DSC. The DTA experiment is performed in a temperature range from 20 to 1000°C with a heating rate of 15°C/min under a 99.995% Ar flow. A mass of 6.35 mg of an Al/NiO nEM is carefully scratched from the substrate and put into a platinum crucible. The DSC experiment is carried out at a temperature range from 20 to 700°C at a heating rate of 5°C/min under a 99.999%  $\text{N}_2$  flow with a sample mass of 2.3 mg. Both for the DTA and the DSC, a second analysis is done on the same sample and in the same conditions in order to help with computations of the baseline correction.

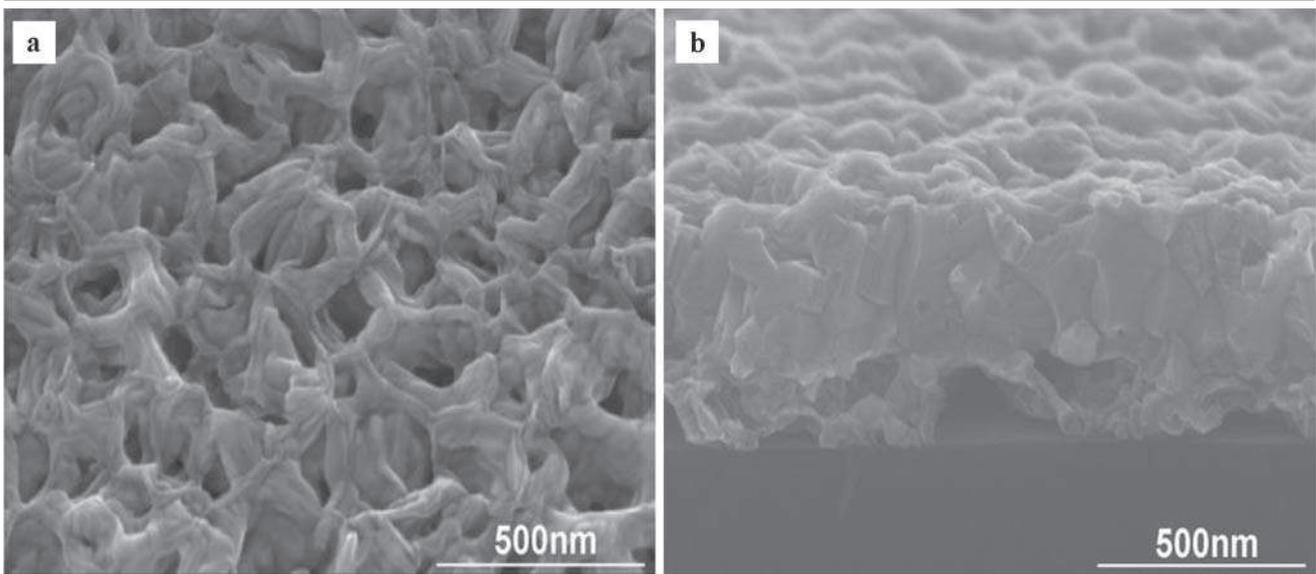
## 3 Results

### 3.1 SEM characterization

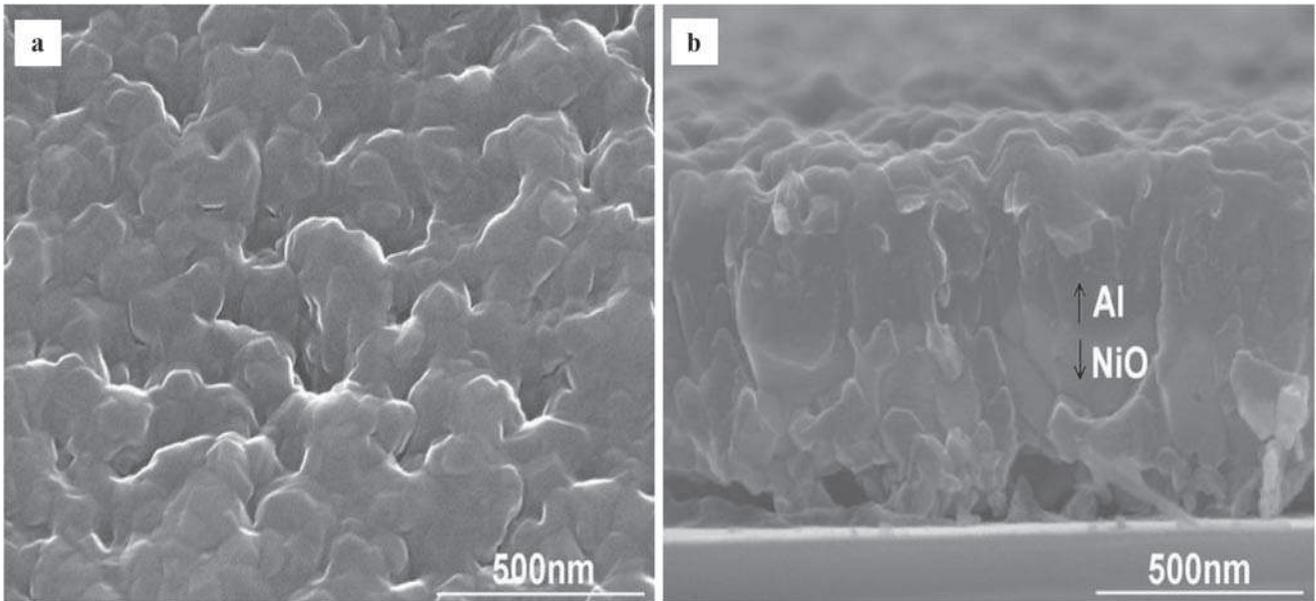
Figure 1a shows a 30° tilted view SEM image of the deposited 0.2- $\mu\text{m}$ -thick Ni thin film onto a silicon substrate by thermal evaporation. The diameter of the deposited Ni particles on the film surface is in the range of 5–15 nm. A cross-sectional view SEM image of the deposited Ni thin film is



**Fig. 1** SEM images of the deposited 0.2- $\mu\text{m}$ -thick Ni thin film by thermal evaporation: (a) a 30° tilted view and (b) a cross-sectional view



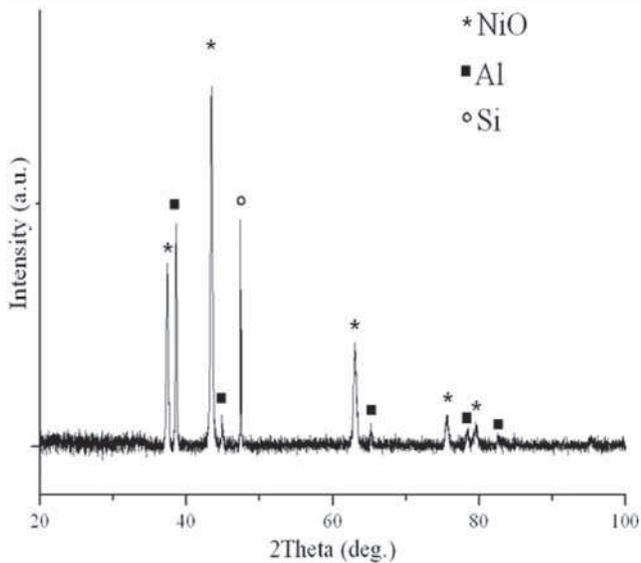
**Fig. 2** SEM images of the annealed Ni thin film at 450°C for 2 h under a  $N_2/O_2$  gas flow: (a) a 30° tilted view and (b) a cross-sectional view



**Fig. 3** SEM images of the annealed Ni thin film after Al deposition: (a) a 30° tilted view and (b) a cross-sectional view

shown in Fig. 1b. Figure 2a is a 30° tilted view SEM image of the annealed Ni thin film for 2 h at 450°C under the  $N_2/O_2$  gas flow. The surface morphology is considerably changed after the thermal annealing. The thin film becomes porous and honeycomb-like structure is formed with a wall thickness of 50–150 nm. Experiments also show that relatively uniform nano honeycomb can be created on the entire surface film deposited on a 4-inch silicon wafer. Therefore, it is suitable for batch fabrication and mass production. Figure 2b shows a cross-sectional view image of the annealed thin film. It can be seen that some of the nano holes extend

through the entire thickness of the thin film. The resulting film thickness is increased by more than two times due to the created porosity. Figure 3a and b show the 30° tilted view and cross-sectional view SEM images of the nano honeycomb after Al deposition, respectively. The deposited thickness (on the average across the sample) of an Al is set to be 0.21  $\mu m$  in the thermal evaporator. By comparison with Fig. 2a and b it can be seen that an Al is intimately integrated with the nano honeycomb, thus enhancing the interfacial contact area between the Al and the nano honeycomb.



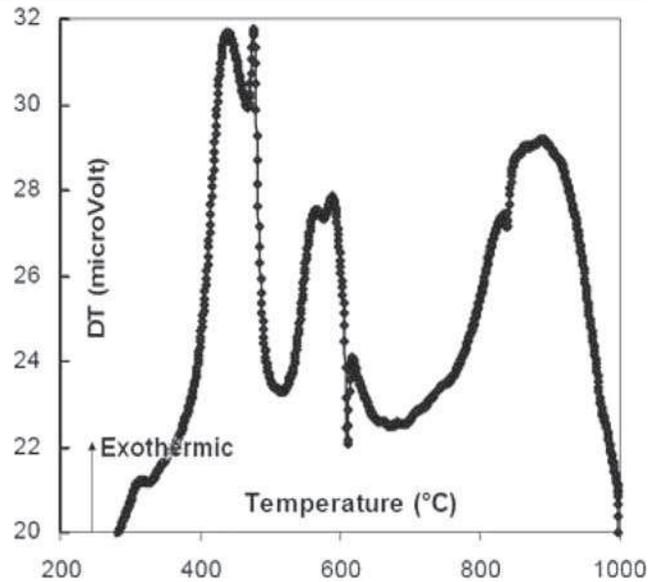
**Fig. 4** The XRD pattern of the Al/NiO nano energetic material before the reaction

### 3.2 XRD characterization before reaction

The as-prepared Al/NiO based nEM is characterized by XRD as shown in Fig. 4. Al and NiO diffraction lines can be clearly seen from the XRD pattern. The diffraction lines for Si are due to the well-crystallized silicon substrate. There are no peaks for Ni in the XRD pattern, indicating that the entire 0.2- $\mu\text{m}$ -thick Ni thin film is oxidized into a pure NiO after heating for 2 h at 450°C under a  $\text{N}_2/\text{O}_2$  gas flow. There are also no peaks for the  $\text{Al}_2\text{O}_3$  in the XRD pattern. This means that neither a significant oxidation of an Al nor the reaction between Al and NiO occur during the Al deposition because of the high vacuum level and low silicon substrate temperature in the thermal evaporator.

### 3.3 DTA characterization

The exothermic reaction of the Al/NiO nEM is characterized by DTA as shown in Fig. 5, where the deposited Al thickness is 0.21  $\mu\text{m}$ . It can be seen that there are three major exotherms associated with the thermite reaction. The first exotherm is observed with an onset temperature of around 400°C and the second exotherm is found with an onset temperature of around 530°C, which means that the nano energetic composite seems to react prior to the melting of Al. This suggests that the two exotherms are caused by the thermite reaction between the NiO nanostructures and the nano Al. The reactions are based on the solid–solid diffusion mechanism. Thus the ignition temperature of the Al/NiO thermite composite is significantly reduced by creating nanostructured Al and NiO. The increased surface energy of the NiO nanostructures and nano Al enhances their

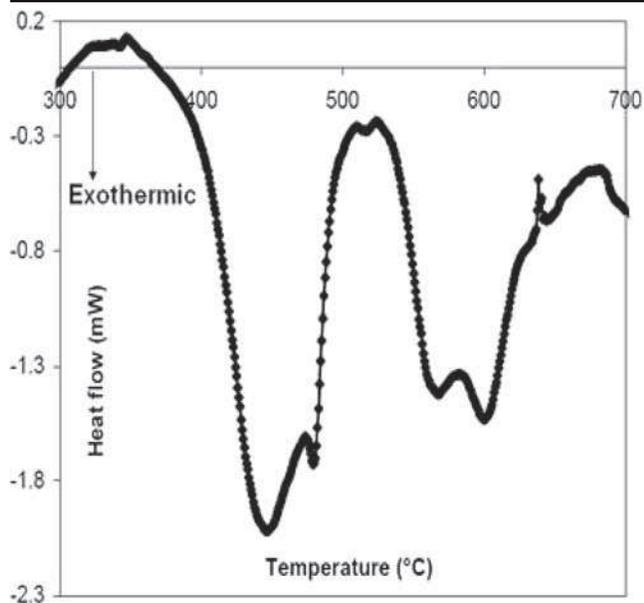


**Fig. 5** The DTA plot of the reaction of the Al/NiO nano energetic material

reactivity and stimulates reduced ignition temperature. Pantoya et al. have also found similar phenomenon that the ignition temperature of a Al/MoO<sub>3</sub> thermite composite is greatly reduced by replacing microparticles with nanoparticles [15]. After melting of Al (giving a sharp endothermic peak above 600°C), the remaining Al reacts with a NiO beneath the NiO nanostructures at an onset temperature of about 800°C. This last reaction occurs by a liquid–solid diffusion mechanism.

### 3.4 DSC characterization

In order to evaluate the heat of the reaction, the Al/NiO nEM is characterized using a DSC with a maximum temperature of 700°C as shown in Fig. 6. The first and the second exothermic peaks with the onset temperatures of about 400 and 535°C are corresponding to the first and the second peaks in the DTA curve in Fig. 5, respectively, which are caused by the solid–solid reaction between the NiO nanostructures and the nano Al. Integration of the two exothermic peaks in the DSC gives a heat of the reaction equal to 1020 J/g. By assuming that the DTA signal is proportional to the heat of the reactions, we can use the area of the two exothermic peaks, calculated from the DSC analysis, to scale the DTA curve. Though it is not accurate, because the relationship between the temperature and the heat is not exactly linear, it allows to roughly estimate the total heat of the reaction of the Al/NiO nEM to be about 2200 J/g. This value is in a similar range with that (1800 J/g) obtained for the Al and MoO<sub>3</sub> nanoparticles based nano energetic material [15]. Both of them are far below their corresponding theoretical values of heat of reactions (3400 J/g for the reaction between Al and NiO, 4700 J/g for the reaction between



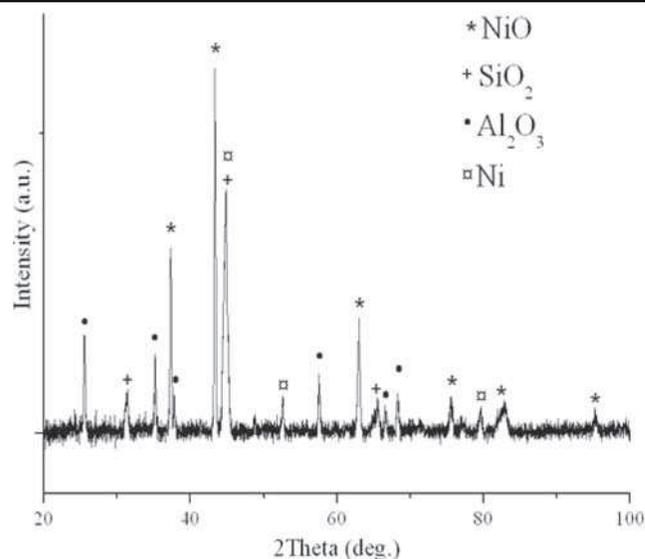
**Fig. 6** The DSC plot for the reaction of the Al/NiO nano energetic material

Al and  $\text{MoO}_3$  [16]). In this experiment, the low heat of the reaction is mainly caused by two factors. One is that the Ar flow used for DTA analysis contains some oxygen (50 ppm) that oxidizes the deposited Al during the heating process. The other is that the masses of Al and NiO in the Al/NiO nEM are not at the stoichiometric ratio.

### 3.5 XRD characterization after DTA testing

Figure 7 shows the XRD pattern of the Al/NiO nEM after a DTA analysis. The final reaction products are identified to be  $\text{Al}_2\text{O}_3$ , Ni, NiO, and  $\text{SiO}_2$ . In this pattern, the Al peaks seen in Fig. 4 before the reaction are no longer present.  $\text{SiO}_2$  is formed from the oxidation of Si scratched from the silicon substrate. The peaks of NiO are probably from the redundant unreacted NiO or due to the oxidation of a part of the reaction product Ni by  $\text{O}_2$  contained in Ar.

The approach employed in this study has several merits compared to previous investigations. First, the Al/NiO nEM is fabricated by integrating nano Al with NiO nano honeycomb grown from a Ni thin film, thus enhancing the interfacial contact area, atomic mixing, and reactivity compared to powders. Second, the increased surface energy of the NiO and Al nanostructures stimulates reduced ignition temperature with a low onset temperature of  $400^\circ\text{C}$ . Third, the presence of impurities and the Al oxidation are much smaller than that in sol-gel or powder mixing processes, because the Al/NiO nEM is fabricated in a high vacuum and with a low substrate temperature. Fourth, since the dimensions of the NiO nano honeycomb can be tailored by adjusting the annealing conditions (temperature, duration, etc.) as stated in [17], the oxidizer/fuel dimensions can be controlled at the



**Fig. 7** The XRD pattern of the Al/NiO nano energetic material after DTA testing

nanoscale. Fifth, the process uses standard microfabrication technologies and therefore it is suitable for batch fabrication and mass production. The Al/NiO based nEM is realized onto silicon that is a basic material for microelectronics and microsystems. Consequently, it is straightforward to integrate the nEM into microsystem. This will result in potential nano based functional structures, for instance, nano energetic material based high performance igniters, as suggested in [18, 19].

## 4 Conclusions

Al/NiO nano energetic material has been realized by integrating nano Al with NiO nano honeycomb grown from a Ni thin film deposited onto a silicon substrate. The Ni thin film is converted into a pure NiO after the thermal annealing. After deposition, Al is intimately integrated with the nano honeycomb, thus enhancing the interfacial contact area between Al and the nano honeycomb. DTA and DSC results suggest that nano Al reacts with NiO nano honeycomb with an onset temperature of about  $400^\circ\text{C}$ . The reaction is based on the solid–solid diffusion mechanism. The total heat of the reaction of the thermite reactions is estimated to be about  $2200\text{ J/g}$ . The realized Al/NiO nano energetic material has the advantages of enhanced interfacial contact area, lowered ignition temperature, reduced impurities, and tailored dimensions. Most interestingly, the Al/NiO nano energetic material is realized onto a silicon substrate, a basic material for microelectronics and microsystems. Therefore, this will probably open the door to integrate the nano energetic material into microsystems, thus leading to functional nanodevices.

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