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# Ni nano-films processed by ammonia

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**Abstract.** The effects of ammonia processing on the nanostructures of nickel catalyst films were researched. The nickel films were prepared by metal vapor vacuum arc (MEVVA) plasma deposition system on $SiO_2$/Si or Si substrate. It was found that the nanostructures of nickel particles were depended on the factors such as the processing time of ammonia, film thickness and the processing temperature. The appropriate processing time of ammonia and the processing temperature are the key factors to obtain high dense, small and uniform Ni nano-particles. $SiO_2$ layer has the effects of preventing the chemical combination between nickel and silicon during the processing period. The influence of ammonia on Ni nano-films was simply discussed.

**Keywords:** Nickel nano-film, ammonia processing, nanostructure

## 1. Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have attracted great attention for their future applications based on their unique physical and chemical properties. Recently, the investigations of field emission flat panel display (FE-FPD) [2] of CNTs have encouraged people to develop a variety of methods to synthesize well-aligned carbon nanotube arrays. Among these methods, chemical vapor deposition (CVD) was adopted broadly for their simple equipments, low cost, easy controllability and high production [3]. The alignment of CNTs fabricated by CVD was considered as the result of van der waals interactions between CNTs [4], so the alignment degree of CNTs can be ultimately attributed to the nanostructures of transition catalyst films on different substrates. Catalyst particles with small diameters, high densities and uniform distribution are favorable for the alignment of CNTs in CVD method.

Up to now, people have employed many different methods such as electron-beam lithography (or photolithography) [5], porous template [6, 7], plasma bombardment [8], excimer laser nanostructuring [9] and thermal ammonia processing [5] etc. to prepare catalyst for synthesis of aligned carbon nanotube arrays. Electron-beam lithography and photolithography are the best techniques for controlling nanostructures of catalyst films, but high cost hindered it from large-scale industrial application; preparation of porous template is relatively complex and can not be completed by one step at the synthesis stage of CNTs; plasma bombardment is just convenient for the method of plasma-enhanced chemical vapor deposition; excimer laser nanostucturing has just been put forward lately and not adopted widely. Thermal ammonia processing may be the most effective, cheapest

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and simplest technique for catalyst film treating. It had been frequently employed. However, systematic researching about the influence of ammonia on the catalyst nanostructures was absent. In this paper, the procedure of continuous nickel catalyst films being thermally transformed into particles as well as the ammonia adjustments on them were investigated detailedly. As a result, we obtained nickel catalyst films with small, high dense and uniform particles.

## 2. Experimental

High pure nickel rod was used as anode of the metal vapor vacuum arc (MEVVA) plasma deposition system [10]. Nickel films with different thickness (2nm, 5nm, 10 nm, and 15nm) were deposited on $SiO_2$/Si or Si substrate. The thickness of $SiO_2$ layer was 30nm. The substrates were polished by Ni plasma bombardment before deposition. Thermal processing for these deposited samples with or without ammonia were carried out in the quartz tube in an electric furnace. Prior to the introduction of ammonia, the nickel films were reduced in hydrogen for 30 minutes. Then, at the rated temperature, ammonia was introduced into the quartz tube for thermal ammonia processing. However, processing without ammonia was fulfilled in hydrogen all along. The processed samples were characterized with a field emission scanning electron microscopy (FESEM) Hitachi S-4300 FEG. Results were analyzed using commercial image analysis software Image-pro plus [11].

## 3. Results and discussion

### *3.1 Formation of nickel nano-particles*

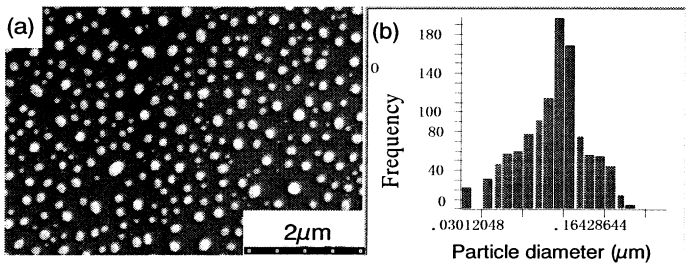


Fig. 1 Nanostructures and size distribution of 5nm nickel films on $SiO_2$/Si surface processed in hydrogen until the temperature just reached 750℃: (a) SEM, (b) particle size distribution.

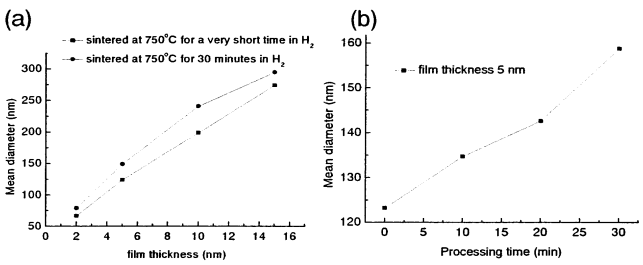


Fig.2 Mean diameter of nickel particles on $SiO_2$/Si substrate vs. the film thickness and processing time, samples were processed in hydrogen at 750℃: (a) mean diameter vs. the film thickness, (b) mean diameter vs. the processing time.

After being processed in hydrogen, the Ni films were transformed from continuity to discrete particles. Fig.1 is the SEM image and size distribution histogram of 5nm Ni films

on $SiO_2$/Si substrate processed in hydrogen until the temperature just reached 750℃. From Fig. 1a, it can be seen that bigger particles are less than small particles, and each bigger one was surrounded by several small ones; Particles lay in lines and all the lines build up a "web"; Size distribution of these particles is monomodal (Fig. 1b) and the mean diameter is 123nm. Processed films with other different thickness have likewise a "web" structure, and their particle size distributions are also monomodal. Based on these results, the formation of nickel particles from continuous films can be conceived. Melting points of metal in nano-size is much lower than that of mass materials [12]. In the course of temperature increasing, nickel nano-films will melt at a certain temperature below its bulky melting point. Due to surface tension, as well as the compressive stress due to the mismatch of the thermal expansion coefficients of Ni and Si/$SiO_2$ [13], molten Ni films contracted and many pinholes appeared. Increasing temperature induced these pinholes grow larger and more pinholes would be produced. The retreating molten nickel film between two pinholes coalesced into a filament. The final structure of the film becomes an array of large droplets connected by a web of filaments. At a slightly higher temperature, these filaments will get enough energy to break up into small droplets.

The statistical results revealed that the final size of nickel particles depend on the initial film thickness and processing times. Fig. 2 showed that the mean diameter of nickel particles increased with the increasing of the film thickness and the processing time in hydrogen at 750℃. Thicker films have larger particles. This should be attributed to the mass increment on the same surface area. The size variation tendency of particles seems to increase linearly according to the processing time as depicted in Fig. 2b. The mean diameter enlarging rate of 5nm Ni films is about 1.18nm per minute. This may be resulted from that the tiny particles was being absorbed by their neighboring bigger ones when the processing was going on.

### *3.2 Ammonia adjustment to the nanostructures of nickel particles*

#### *3.2.1 Influence of ammonia on the structures of Ni particles at 750 ℃*

Fig. 3 is SEM images of 5nm nickel film processed by ammonia at 750℃ for 4, 6, 8, 10, 12 and 20 minutes respectively. These pictures showed that the Ni particles have experienced a procedure of size variation after ammonia was introduced into the quartz tube. After analyzed by Image-pro plus, their mean diameter variations were drawn as curve (a) in Fig. 4. Based on the curve's undulation, the size variations of Ni particles can be divided into four stages as labeled in the figure. At the first stage (A-B), ammonia was just introduced into the quartz tube. It was less in the mixture gas and could not change the particle size remarkably. Thermal diffusion of atoms was the main influencing factor of the particle size at this stage, so they grew larger gradually. At the second stage (B-C), the concentration of ammonia in the mixture gas was increased enough to diminish the Ni particle size. The diminishing mechanism of ammonia may be considered as two aspects: First, diffusion and surface absorption of species and radicals from ammonia on the interfaces between the mixture gas and the nickel droplets handicapped nickel diffusion on $SiO_2$/Si substrate, it was more difficult for large particles to assimilate their neighboring tiny ones; Second, these species and radicals with high kinetic energy would act on the defects of nickel particles, such as grain boundaries, and made them smaller [13]. The

second stage will last until about 10 minutes after the introduction of ammonia as the nickel particles had a minimum of the mean diameter and a maximum of the density. At the third stage (C-E), prolonging the processing time of ammonia meant that nickel atoms would have gotten enough time to diffuse on the substrate; the particles resumed their sizes by assimilating each other slowly. At the fourth stage, there is no obvious alteration in particle size. Ammonia diminishment and the assimilation between Ni particles appeared to reach a homeostasis at this stage. The mean diameter will hardly change with the processing time of ammonia at/after this stage. Though there need more investigations to determine the etching mechanism of ammonia on Ni films, films with other thickness have the same variation tendency of the mean diameters as the 5nm film, except the location height of their curves.

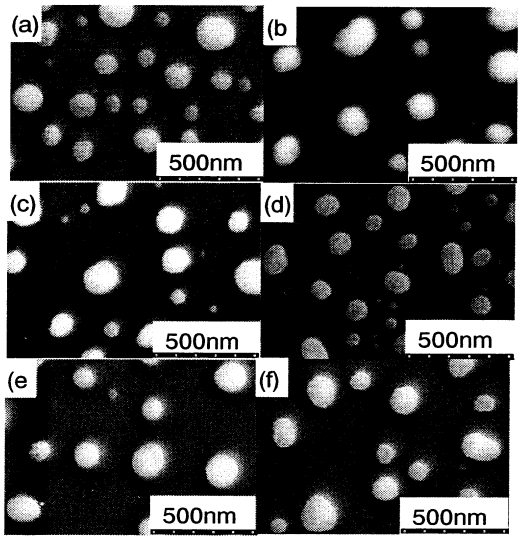


Fig. 3 SEM images of 5nm nickel film on $SiO_2$/ Si surface processed by ammonia at 750℃ for different time: (a) 4 min., (b) 6 min., (c) 8 min., (d) 10 min., (e) 12 min., and (f) 20 min..

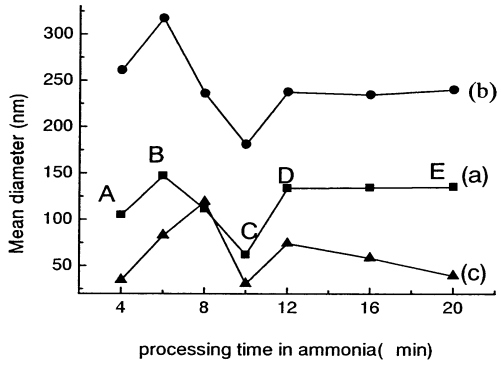


Fig. 4 Mean diameter variation curves of nickel films processed by ammonia at 750℃: (a) 5nm Ni films on $SiO_2$/ Si substrate, (b) 10nm Ni film on $SiO_2$/ Si substrate, (c) 10nm Ni films on Si substrate

The variations of the mean diameter of nickel particles vs. the film thickness after ammonia processing at 750℃ were depicted in Fig. 5. The curves showed that the particle sizes increase monotonically with the increasing of the film thickness even after processed thermally by ammonia; therefore, it is not adoptable to increase the particle densities by increasing the initial film thickness in thermal ammonia processing.

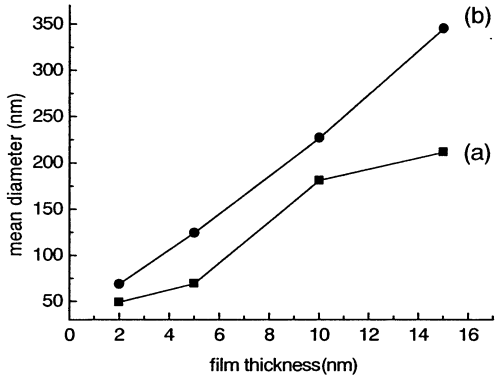


Fig. 5 Size of nickel particles on $SiO_2$/Si substrate increases with the film thickness processed by ammonia at 750℃ for different times: (a) 10 min., (b) 20 min..

### *3.2.2 Influence of processing temperature*

Altering ammonia processing temperature will also change the nanostructures of nickel films on the substrates. Fig. 6 are SEM images of 10nm Ni films on $SiO_2$/Si substrate processed by ammonia for 10 minutes at 650℃, 750℃, 850℃ and 950℃ respectively. Statistical results of their mean diameters were plotted in Fig. 7. Comparing the images of Fig. 6, it can be concluded that the Ni particles diminished as well as their densities increased with the increasing of processing temperature, this should be attributed to the enhanced diminishing ability of ammonia species and radicals which have gotten more kinetic energy at the elevated temperature. On the other hand, the diffusion ability of nickel atoms have also been increased simultaneously at the higher temperature and it is easier for nickel droplets to agglomerate into large ones. Therefore, Fig. 6 (d) exhibited a morphology of large Ni droplets dispersed on a background of numerous extremely tiny ones. Fig. 6 and Fig. 7 elucidate that elevating the processing temperature can diminish the nickel particles, but the uniformity of them become worse at extra high temperature. Only proper processing temperature can ensure the small mean diameter and the uniformity of the nickel particles simultaneously.

### *3.2.3 The function of $SiO_2$ layer*

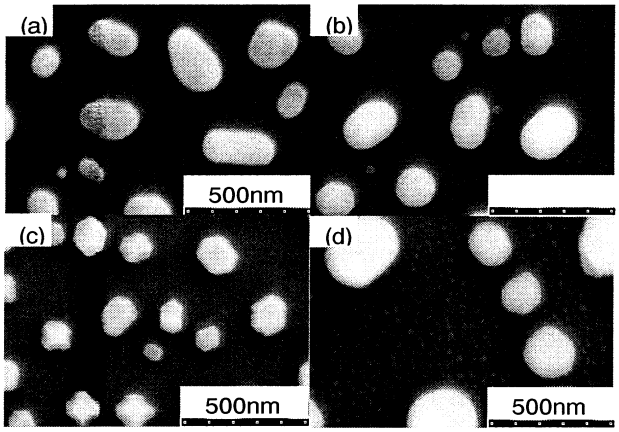


Fig. 6 SEM images of 10nm nickel films on $SiO_2$/Si substrate processed by ammonia for 10 minutes at different temperatures: (a) 650℃, (b) 750℃, (c) 850℃, (d) 950℃.

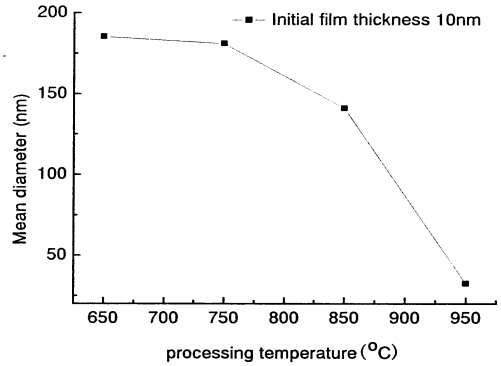


Fig. 7 mean diameter of particles of 10 nm nickel films on $SiO_2$/Si substrate vs. processing temperatures, ammonia processing time was 10 minutes

While the samples which nickel films were deposited directly on Si wafer sintered at 740℃, polycrystalline NiSi compound will be formed. When the temperature rises to 800 ℃, NiSi compound will be transformed into $Ni_2Si$ [14]. The mean diameter variation tendencies of 10nm nickel films on Si and $SiO_2$/Si substrate are showed in Fig. 4 (b) and Fig. 4 (c) respectively. The mean diameter of the nickel particles on Si/$SiO_2$ substrate is larger than that on Si substrate. Furthermore, the slope of the curve (c) is smaller than that of the curve (b) overall, this implied that the combined mass amount of nickel on Si substrate increased with the prolonging time of ammonia processing. It can be concluded that the mass amount of nickel on Si substrate was disappearing during the processing by chemical combination between Ni and Si.

## 4. Conclusion

(1) Nickel nano-particles were transformed from continuous films during the processing period in hydrogen; their sizes increase with the increasing of film thickness and the processing temperature;

(2) The introduction of ammonia can adjust the nanostructures of these nickel particles, proper processing time and temperature of ammonia is the key factors to obtain nano-particles with small sizes, high density and excellent uniformity;

(3) $SiO_2$ layer on Si substrate prevented the disappearing inclination of the nickel particles by handicapping the chemical combination between nickel and silicon during the thermal ammonia treatment.

## Acknowledgement

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