Formation of Three Dimensional Ni Nanostructures for Large Area Catalysts

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ABSTRACT

The formation of Ni nanostructures to act as catalysts in the growth of carbon nanotubes is reported. The changes in the surface morphology of Ni produced by three methods - thermal evaporation and annealing of thin films, pulsed laser ablation and annealing of Ni, and the use of metal containing macromolecules - have been investigated by atomic force microscopy and scanning electron microscopy. In the case of thermal annealing of thin metal films in the temperature range 300-500°C we observe an increase in the mean diameter of the islands formed, accompanied by a reduction in the mean island density with increasing temperature. We attribute this effect to mass transport of weakly bound individual Ni atoms and/or small island clusters across the surface to form larger isolated islands, in a process similar to Ostwald ripening. Using a pulsed KrF excimer laser for ablation of a Ni target we show that nanometre smooth Ni thin films can be produced provided a sufficient number of laser shots is used. The surface morphology of these smooth films can then be altered by laser annealing to form Ni droplets. It is found that the mean diameter of the Ni droplets depends not only on the initial Ni thickness but also the laser fluence. It is also found that the nanostructuring of the film depends on the presence of an oxide under layer, with a higher fluence required on thinner oxides and no nanostructuring observed on bare Si. Finally, we show that Ni nanostructuring can be formed by suitable annealing of a Ni containing aqueous dendrimer solutions.

INTRODUCTION

Future applications in large area electronics may, ironically, be driven by a greater understanding of material systems at a nanometre level. To that end, the preparation of large area substrates, ideally at low temperatures (<600 °C), that can be used either directly or as catalysts for subsequent growth is extremely important. Carbon nanotubes (CNTs) is one material system where an ability to grow over large areas may lead to significant developments towards the next generation of wide screen field emission based flat panel displays [1]. The controllable growth of CNTs is, however, often determined by properties such as mean catalyst diameter, distribution of the catalyst across the substrate and the mutual interaction between the growing nanotube, the catalyst and the substrate itself [2]. This is in addition to the changes in process parameters such as type and flow rates of source gases, growth temperature and pressure. The latter quantities are readily determined by the user, and as a result an ability to predetermine the catalyst properties before growth is important. This proposition holds true for both conventional large area catalysts and also for catalysts defined lithographically. In this study we use thin Ni metal and three different techniques to alter its morphology – thermal annealing of thin films, pulsed laser ablation to produce the film and then laser annealing to alter the film and an aqueous macromolecular solution than can be spin coated.

EXPERIMENTAL METHOD

For the annealing of thin metal films, substrates of *n*-Si were initially cleaned using a standard three stage ultrasonic solvent clean. A layer of Ti 100 nm thick was evaporated on the substrates by heating Ti metal in a vacuum of 4×10^{-6} Torr. The films were then subsequently oxidized in air by annealing for 30 minutes. Ni films were then evaporated using high purity Ni wire which were subsequently annealed under flowing N₂ at temperatures from 300°C up to 500°C for times of 10, 30 and 60 minutes.

For pulsed laser ablation studies, thin Ni films were produced by multiple laser shots (10–2000) of a Lambda-Physik LPX 200 Excimer laser operating at 248 nm at a fluence of 10 J/cm² onto a 99.9% pure Ni target. Further details can be will be published elsewhere [3]. The substrates used were SiO₂/Si with either native oxide coverage or with a thermal oxide of 235 nm or 320 nm thickness. Laser annealing of the resultant thin films was performed using the same excimer laser as for growth. The samples were attached to a translation stage and annealing in vacuum was performed by translating the stage at 1 mm/s with a laser repetition rate of 10 Hz. For the annealing studies, laser fluences from 100 to 300 mJ/cm² were used.

Finally, dendrimers, which are metal containing macromolecules, were prepared from commercially [4] available polyamidoamine 6th Generation dendrimer solution with 100 % OH terminated surface groups. Using 48 µL of 17.83 % wt. of dendrimer mixed with 100 µL of 0.1 M NiCl₃ · 6 H₂O, a 10 ml solution was obtained using double distilled water. A low concentration was formed by diluting the stock solution 100 times. Silicon substrates with native oxide were soaked in the diluted dendrimer solution for 5 seconds, rinsed with double distilled water to remove poorly attached or polymerised dendrimers from the substrate and blown dry with nitrogen. The substrates were annealed in a vacuum of 10⁻³ Torr at 650 °C for 5 minutes.

The surface morphology of all the substrates were examined using atomic force microscopy (either a Digital Instruments Nanoscope IIIa or a Dimension 3100 microscope). Scanning electron microscopy using a Hitachi S4000 field emission gun scanning electron microscope (SEM) was also employed.

RESULTS AND DISCUSSION

Thermal annealing of thin metal films

High resolution AFM measurements (not presented here) of the unannealed Ni films with a thickness of 8 nm show that the surface of the film to be extremely flat. However, the surface morphology changes upon annealing for 30 minutes as shown in Fig. 1. After annealing at 300 °C, modulations of the surface can be see with evidence of small localised islands present. Annealing at 400°C (Fig. 1 (b)) produced larger islands with an irregular shape and a mean diameter of 114 nm. The increase in the mean size of the islands is coupled with an increase in the larger inter-island spacing. This increase in the mean size and separation is further seen after annealing at 500°C. In this case, large diameter islands (average diameter of 306 nm and a standard deviation of 97 nm) can be seen in Fig. 1(c), and the resultant islands are also more isolated from each other. The results shown in Fig. 1 demonstrate that annealing at successively higher temperatures results in the formation of isolated large diameter islands at the expense of smaller close packed islands.

Figure 1. Surface morphology of three 8 nm Ni films annealed for 30 minutes at (a) 300 °C, (b) 400 °C and (c) 500 °C. The scan sizes are 4 μm x 4 μm.

Although the deposition of Ni results in compressive strain on the oxidised titanium, the strain energy is not substantially reduced through thermal annealing since the coefficients of linear expansion [5] for Ni and the oxide, taken to be $13.4 \times 10^{-6} \text{ K}^{-1}$ and $7.14 \times 10^{-6} \text{ K}^{-1}$ respectively, are similar. The effect of annealing at high temperatures is to allow mass transport of either individual Ni atoms or small clusters across the surface in which larger clusters can be formed out of smaller clusters in a process analogous to Ostwald ripening. Such a process is consistent with the low interaction of Ni atoms on oxide substrates. Metals which possess high heats of formation of the oxide react strongly with the substrate and produce flat 'wetting layers'. The heats of formation of the oxide, $-\Delta H$, are $\sim 5.2 \text{ eV}$ for Ti and 2.49 eV for Ni [6]. Since the value of $-\Delta H$ for Ni is about half that of Ti, the growth of Ni will result in little interaction with the substrate. As a result low barriers of atom diffusion on the surface are possible. Further confirmation of a surface diffusion hypothesis leading to larger islands can be found from the examination of the island density inferred for the AFM measurements. On thermal annealing, the density of islands decreases from $32.6 \mu\text{m}^{-2}$ at 300°C, to $15.6 \mu\text{m}^{-2}$ at 400°C and to only $2.3 \mu\text{m}^{-2}$ after annealing at 500°C.

For thinner metal layers of 3 nm and 5 nm it was found that after annealing at 400 °C for 30 minutes island formation has occurred but with mean diameters of 67 nm and 89 nm respectively. These values can be compared to 114 nm found for 8 nm thick. Annealing studies at 10 and 60 minutes produced similar results from which we conclude that the two most important aspects in producing Ni islands are the annealing temperature and the initial Ni layer

thickness. Annealing at higher temperatures produces larger diameter islands though further in distance from one another. The weak interaction between the Ni and the oxide layer results in a low activation energy barrier to Ni migration which results in larger islands forming from smaller islands. In this way the kinetic factors which affect mass transport and surface diffusion of material are an important consideration in addition to simple thermodynamic factors since metal-on-oxide often represents a far from equilibrium system [7].

Laser ablation, annealing and droplet formation of Ni nanostructures

The initial stages of growth of the Ni films by laser ablation onto a 320 nm thick SiO₂ on Si substrate was investigated using AFM. Figure 2 shows the evolution of the surface after 10, 50 and 200 laser shots at a fluence of 10 J/cm². The scan sizes are 400 nm x 400 nm in each case.

Figure 2. AFM images of laser ablated Ni for (a) 10 (b) 50 and (c) 200 laser shots at 10 J/cm².

For a low number of laser shots (10 shots), the surface is not continuous, however, film continuity begins to emerge at around 200 shots and by 1000 shots a smooth film with a root mean square roughness of less than 1 nm emerged. By masking a section of the substrate prior to deposition, it was possible to measure the Ni film thickness by scanning the AFM over the step produced. 750 laser shots produced a film 6.5 nm thick and 1500 shots resulted in a thickness of 8.2 nm.

Figure 3 shows series of SEM images of a selection of the laser annealed films, with different initial Ni thickness, grown on 320 nm SiO₂/Si substrates annealed with a laser fluence of 160 mJ/cm². After annealing the Ni film was observed to break up into discrete nanometer-scale hemispherical islands – metal droplets.

Figure 3 SEM images of three films with thickness (a) 6.5 nm (b) 8.2 nm and (c) 12 nm annealed at a laser fluence of 160 mJ/cm². The error in film thickness is ± 1 nm.

At fluences below a critical value (which was dependent on the Ni thickness), the films were observed to perforate, but droplet formation did not occur. For fluences above 280 mJ/cm^2 significant ablation of the Ni was observed for all Ni film thicknesses investigated. Whilst it was observed that at intermediate fluences the Ni island size was unaffected by the laser fluence, the fluence required to achieve droplet formation does depend on the thickness of the oxide layer on the substrate. The fluence required to nanostructure the films grown on the thinner (235 nm) thermal SiO_2 substrates was higher than for the corresponding Ni film on the thicker SiO_2 layers.

On the Si substrates with only the native oxide layer, no nanostructuring was observed for fluences below the ablation threshold of the film. This attributed to the higher thermal conductivity of Si ($150 \text{ Wm}^{-1}\text{K}^{-1}$) when compared with that of SiO_2 ($1.34 \text{ Wm}^{-1}\text{K}^{-1}$). [5] It can be observed that the mean droplet size increases as the initial film thickness increases, which is consistent with the thermal annealing data of thin films, shown in Fig. 1. However, unlike the Ni island formed by thermal annealing the Ni droplets formed here are prepared without any macroscopic heating of the substrate.

Ni nanostructures from dendrimer macromolecules

Figure 4(a) shows an AFM image of the surface of Si substrate on to which dendrimers have been adsorbed by soaking in the diluted solution and subsequent drying. The surface consists of circular features with a diameter of few tens of nanometres. After thermal annealing at 650°C for 5 mins evidence of coalescence of the dendrimers into larger features is observed, Fig. 4(b).

Figure 4 AFM image of (a) the dried as-grown dendrimer and (b) annealed at 650°C for 5 minutes.

By using a combination of high resolution transmission electron microscopy and energy dispersive X-ray analysis it has been shown that the nanostructure also consists of Ni particles surrounded by a thin (3-5 nm) carbon shell. The presence of the C shell surrounding the Ni has a benefit over a bare Ni surface since the carbon acts as a barrier to diffusion of the metal atom into the silicon substrate, at high temperatures, and inhibits the formation of a silicide. This results in the growth of mats of CNT over large areas [8].

CONCLUSIONS

In this paper we have demonstrated the formation of Ni nanostructures using conventional thermal annealing, laser annealing, and annealing of metal containing macromolecules. For a given metal thickness, conventional thermal annealing results in the formation of a smaller number of larger diameter metal islands. The thermal energy supplied to the whole of the film results in the transport of smaller islands to form larger islands. Smooth Ni thin films can be produced from laser ablation of a Ni target which can then be nanostructured by pulsed laser annealing. The laser fluence needed to form Ni droplets depends on the thermal conductivity of the underlying substrate, and higher fluences were required on thinner oxides with no nanostructuring also observed on bare Si. Finally, we have demonstrated that annealing of Ni dendrimers can result in Ni nanostructures. This final approach allows the use of an aqueous solution than is compatible with spin coating technology and may provide a way to produce large area catalysed substrates.

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