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Domain growth of carbon nanotubes assisted by dewetting of thin catalyst precursor films

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ABSTRACT

We explore self-organized dewetting of ultrathin films of a novel metal complex as a one step surface patterning method to create nanoislands of iron, using which spatially separated carbon nanostructures were synthesized. Dewetting of ultrathin metal complex films was induced by two different methods: liquid solvent exposure and thermal annealing to engender surface patterning. For thermal dewetting, thin films of the iron oleate complex were dewetted at high temperature. In the case of liquid solvent assisted dewetting, the metal complex, mixed with a sacrificial polymer (polystyrene) was spin coated as thin films (<40 nm) and then dewetted under an optimal solution mixture consisting of methyl ethyl ketone, acetone and water. The carrier polymer was then selectively removed to produce the iron metal islands. These metal islands were used for selective growth of discrete patches of multiwall CNTs and CNFs by a chemical vapor deposition (CVD) process. Solvent induced dewetting showed clear advantages over thermal dewetting owing to reduced size of catalyst domains formed by dewetting, an improved control over CNT growth as well as in its ability to immobilize the seed particles. The generic solution mediated dewetting and pattern generation in thin films of various catalytic precursors can thus be a powerful method for selective domain growth of a variety of functional nanomaterials.

1. Introduction

Carbon nanotubes (CNTs) have been amongst the most intensively studied and used 1-D nanostructures since their discovery in 1991 [1]. Owing to their unique and technologically promising properties like high chemical and thermal stability, high tensile strength and peculiar electronic transport properties [2–4], they have dominated the research field of carbon related materials in recent decades. Many applications of nanotubes require micro-patterning and control over the location of the nanotubes on a substrate [5]. This is important for applications in sensors and batteries where non-interacting micro-domains of CNTs are required [5–8]. Since the growth of CNTs is seed mediated, the control can be achieved by using surface patterning of catalyst nanoparticles (Fe, Co or Ni) which act as seeds of CNTs. The patterns of nanoparticles on the substrate can thus be transformed into patterned CNT growth by CVD synthesis under suitable growth conditions.

Most of the available techniques involve deposition of catalyst layer by physical [9] or pulsed laser vapor deposition [10] and patterning by lithography based techniques like E-Beam or photolithography [11–13], dip pen lithography [14], direct printing techniques [15] and other methods [16,17]. These top-down methods are slow and expensive for large area patterning. Other methods involve chemical preparation of the nanoparticles and their immobilization on specific sites over the substrate [18]. Here we explore a novel and easy approach to fabricate isolated micro-domains of seed nanoparticles keeping in view the need for a low cost and high throughput method for large area patterning.

The chemical approach to synthesizing iron nanoparticles exploits reduction of metal salt in presence of capping agents [19,20]. This results in stable dispersions of nanoparticles in specific solvents. Self-assembly of nanoparticles on a substrate has also been previously explored [20]. However, the high temperature CVD process introduces several difficulties including uncontrolled thermal movement of nanoparticles, degradation of capping agents, particle aggregation, etc. all of which make particle immobilization at selected sites nearly impossible.

Here we report *in situ* formation of micro-domains of immobilized nanoparticles on silicon wafers by dewetting of thin films of an iron-oleate complex with or without a sacrificial carrier polymer. The complex used is soluble in low volatility solvents like *n*-hexane and toluene, allowing spin coating of its thin films. Further, a polymer solution can be blended with this complex to form a composite film which, as discussed below, can be dewetted by exposure to

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a liquid solvent. Thermal annealing transforms micro-domains of iron-oleate precursor complex into domains of iron nanoparticles, from which CNT are grown by a CVD process.

Dewetting of an unstable thin liquid film on a substrate proceeds by the breakup and retraction of the polymer to eventually form discrete islands [21–23]. The mobility of molecules required for dewetting occurs beyond the glass transition temperature which can be achieved by various means such as exposure to solvent vapor, thermal annealing and immersion into a solvent–non solvent mixture [24–28]. Characteristic length scale of dewetting (average diameter and spacing of the islands produced by dewetting) depends on surface tension and film thickness; the latter determining the destabilizing force such as the van der Waals. Thermal dewetting of metal thin films for creating nanoparticles as well as nanoparticle containing thin polymeric films has been previously reported [29–38]. Here, we investigate domain formation by dewetting of both the iron-oleate precursor complex and its composite films with a carrier polymer. Further, dewetting by two different routes, thermal annealing for the iron-complex films and liquid solvent annealing for the polymer-iron complex films are explored to obtain spatially discrete nanostructures for further area selective growth of functional nanomaterials. This generic strategy is demonstrated with the help of CNT growth. An illustrative, quick pre-patterning of the smooth doped films using Capillary force lithography followed by dewetting is also demonstrated in order to obtain CNT growth in a more orderly manner [26,28,39–42].

In what follows, we propose a novel method for large-area fabrication of patterned micro-domains of CNT by using self-organized dewetting of ultrathin (<100 nm) polystyrene film containing an iron oleate complex, which acts as a precursor for the *in situ* generation of iron nanoparticles and subsequent CNT growth by CVD. The sacrificial polymer acts as a delivery vehicle for the positioning of the iron oleate complex in micro-domains and also circumvents the twin problems of iron nanoparticle mobility and aggregation at the elevated CVD temperature. It is also to be noted that the generic technique of dewetting can be combined with a variety of functional growth by choosing the catalyst appropriately. The growth can either be seed particle mediated (in which a completely dewetted polymer contains the catalyst and activates the deposition process upon subjecting to the right growth conditions, for example iron nanoparticles induced CNT growth in this work) or it can be selective surface oriented growth (in which a partially dewetted film acts as a mask for the functional material to be deposited onto the exposed substrate regions, such as growing functional materials on a conducting substrate followed by partial dewetting). In this work, it has been demonstrated that using dewetting, seed mediated growths such as CNT/CNFs can be successfully controlled over a large area.

2. Experimental details

All chemicals used were procured from Sigma–Aldrich and were used without any further purification. Iron complex was synthesized by modifying the method reported by Park et al. [20]. Briefly, 12 mmol of $FeCl_3{\cdot}6H_2O$ was taken in 12 ml DI water solution and mixed with 36 mmol of sodium oleate in a solution of 24 ml ethanol, 6 ml DI water and 42 ml *n*-hexane. The mixture was kept at 70 °C under continuous flow of Argon for 4 h. The mixture phase separated into two layers and the upper brownish layer was removed using a separatory funnel and washed thoroughly with DI water. The resulting solution was dried at 40 °C in vacuum for 3 h leading to a waxy solid which was stored for further experiments. To maintain the consistency of the samples, a stock solution of 1% by weight was prepared in *n*-hexane or toluene and was used in appropriate amounts in all the experiments.

Silicon wafers used as the substrates were obtained from Wafer World Inc. and were cleaned by ultrasonication in TCE, acetone and methanol for 10 min each in that order. Substrates were then kept for a dehydration bake on a hot plate at 200 °C for 30 min after a thorough washing in DI water.

For thermal dewetting, iron complex was spin coated at different spin speeds. The concentration of the iron complex was kept constant in all the experiments as mentioned above. After spin coating, the samples were subjected to annealing at 750 °C for 20 min in an inert atmosphere for thermal dewetting. Scanning electron microscopy was used to determine the nanoparticle size after annealing.

The following process was followed for solvent dewetting. Polymer chosen for solvent induced dewetting was polystyrene (average MW 280,000 and PDI < 1.1). Solution of PS were prepared in HPLC grade toluene (concentration 0.4%, w/v) and doped with the iron complex. Different dosage of complex resulted in varying number density of the CNT growth owing to the varying sparsity of the iron nanoparticles islands. Films were spin coated at 3000 RPM providing a film thickness ~20 nm. Dewetting of these Iron-PS blend films was induced under an optimum mixture of MEK, acetone and water in the ratio of 7:3:15, respectively. Dewetting under this solution is further aided by a stronger destabilizing potential due to presence of water, a highly polar medium. Compared to dewetting in air, water and organic solvents create an ambience which has lower surface tension restrictions. MEK being a good solvent of PS, diffuses into the polymer matrix, resulting in low viscosity of polymer chains. This brings down the T_g of polymer to room temperature and films start to rupture by forming dry spots. Retraction of material from these dry spots gives way to formation of a web like structure which further collapses to generate isolated micro droplets of PS containing iron complex which are somewhat evenly spaced. Due to doping of films, kinetics of iron complex-PS film dewetting is slower than a pristine PS film (takes ~1 h to dewet compared to a few minutes for the same undoped film).

For growing CNTs, following method was adopted. The samples were kept over a quartz plate and inserted inside a 2″ diameter CVD furnace tube. Samples were heated in a constant flow of He (200 sccm) to the temperature of 400 °C at a heating rate of 10 °C per minute. Keeping the heating rate constant, H_2 was introduced at this time (30 sccm) and continued till the temperature reached 750 °C. After this, flow of C_2H_2 (20 sccm) was introduced for 20 min. The furnace was then cooled to ambient temperature, maintaining the constant flow rate of He.

The above method based on dewetting of uniform films creates micro-domains that have well defined mean size and spacings but do not have a spatial order. The methodology described below was used for the creation of ordered catalyst domains. A faint surface pattern was created in the polymer films to guide the self-organized dewetting along preferred directions. The surface patterning was achieved by the capillary force lithography (CFL) technique followed by dewetting. CFL is a standard surface patterning technique in which the film is heated above its T_g when in contact with soft master containing a surface relief pattern [39,40]. The polymer flows in the grooves of the master owing to the capillary effect, which upon cooling creates a periodic structure on the surface of the film.

The master template used was PDMS replica of the CD pattern (channel periodicity ~1.5 μm and depth ~120 nm). These were transferred onto smooth iron doped films of PS at 130 °C for 5 min followed by cooling. Resulting imprinted patterns were then dewetted to obtain aligned nanoislands which were then subjected to CNT growth at optimized conditions. A schematic representation of the experimental protocol is drawn in Fig. 1.