This paper reports on the success in and the key conditions for direct growth of carbon nanotubes of unprecedented uniformity on silicon. The uniformity is ensured through the growth within the highly ordered nanopores of an alumina oxide template, which is in turn formed on silicon through anodization of aluminum of unprecedented thickness evaporated on silicon. The formation of highly ordered nanopore array by anodization of thick aluminum evaporated on a noncompliant substrate such as silicon is made possible through a specially designed process for evaporating thick aluminum of high quality and good adhesion.
Template-Growth of Highly Ordered Carbon Nanotube Arrays on Silicon

Aijun Yin, Marian Tzolov, David A. Cardimona, and Jimmy Xu

Abstract—This paper reports on the success in and the key conditions for direct growth of carbon nanotubes of unprecedented uniformity on silicon. The uniformity is ensured through the growth within the highly ordered nanopores of an alumina oxide template, which is in turn formed on silicon through anodization of aluminum of unprecedented thickness evaporated on silicon. The formation of highly ordered nanopore array by anodization of thick aluminum evaporated on a noncompliant substrate such as silicon is made possible through a specially designed process for evaporating thick aluminum of high quality and good adhesion.

Index Terms—Anodic aluminum oxide template, carbon nanotubes (CNTs), silicon.

I. INTRODUCTION

C ARBON nanotubes (CNTs) have attracted much attention since their discovery (or rediscovery) by Iijima in 1991 [1], thanks to their remarkable electronic, optical, and mechanical properties, and their potential applications [2], [3]. Uniformly sized and spaced arrays of vertically aligned CNTs [4]–[6] are highly desirable for many applications, including field-emission, microelectronics, electrochemical probes, molecular interfaces, and microfluidic devices. One way to synthesize vertically aligned and densely packed uniform CNTs that are spatially isolated from each other is to use a growth template. Highly ordered anodic aluminum oxide (AAO) template can be obtained from Al anodization [7]. Such a template has been used for freestanding film of CNT arrays [8], [9]. It offers the possibility of tailoring the size and density of the nanotubes over a wide range. However, such CNT arrays grown in freestanding AAO/Al templates are limited in applications because they are not readily interfaced electronically with external circuits. Integrating such highly ordered CNT arrays onto Si substrates will broaden their applications and provide possibilities for incorporating CNT material properties or functionality with the Si electronics. This could perceptibly be done by growing CNTs in a highly-order nanopore array template formed directly on silicon. Though formation of AAO in evaporated or sputtered Al film on a Si substrate itself has been shown possible [10]–[12], attempts to grow highly ordered CNT arrays in this structure have met with little success partly because of the need for, and the difficulty in, forming thick enough high-quality Al on silicon and because of the added challenge in keeping such a thick film on a noncompliant substrate from peeling off in the subsequent anodization step or the high-temperature CNT growth. It is likely for this reason, we believe, that there has been no prior report on growth of highly ordered nanotube arrays in an alumina template on silicon. Compared with the successful formation of highly ordered thin AAO films on silicon by anodization of a thin Al film nanoimprinted either by mold pressing or lithographical methods [13]–[16], making avail of a direct anodization approach would present a significant advantage by virtual of eliminating one set of processing steps that are both demanding and costly.

In this paper, we show that: 1) highly ordered arrays of nanopores can be formed by self-organization in anodization of a thick Al evaporated directly on silicon and 2) subsequent growth in the nanopore template can yield vertically oriented CNT arrays of unprecedented uniformity directly on Si substrates. To this end, we deployed a specially designed process of e-beam evaporation, optimized the deposition conditions for obtaining thick Al films with good adhesion to the Si substrate, and developed a timed anodization process that seems to work reliably. This success is expected to lead to many applications in nanoelectronics over and beyond CNTs that would benefit from the direct electronic interface with silicon enabled by this approach.

II. EXPERIMENT

For depositing thick (up to 50 μm) and high-quality Al film on silicon, conventional e-beam evaporation procedure and evaporators are found to be inadequate because of the limitations in the evaporation rate and total amount and oxidation during a long deposition or multiple evaporations. To counter this problem, we used a specially designed high vacuum e-beam evaporator that is equipped with a custom-made substrate holder, featuring temperature control and axial rotation to allow in situ annealing with minimal oxidation and high film uniformity. In order to ensure good adhesion during the anodization, a thin layer (<5 nm) of Ti between Al and Si was predeposited in the case of the thick Al films.

Anodization of the evaporated Al film was carried out using a two-step method [7]. At the end of the anodization process, there is a barrier layer at the bottom of the pores which can be
removed either by chemical wet-etch using 0.5 M phosphoric acid or by dry-etch using chlorine-based gases.

CNT growth within the arrayed nanopores was then carried out by the same chemical vapor deposition (CVD) method as first demonstrated in 1999 and refined over the years [8]. Controlled exposure of the CNTs from the AAO template can be achieved by applying a combination of dry-etching and wet-etching processes, to obtain a given length while keeping the extruded nanotubes from bundling into haystacks [17].

III. RESULTS AND DISCUSSION

To obtain high-quality thick Al films on silicon, we experimented with various deposition conditions, including the substrate temperature (up to 623 °C), the evaporation rate, and the sample cooling rate. High-quality Al films with thickness of 50 μm on Si substrates were achieved, as evidenced in the anodization results presented below, by finely tuning several key deposition conditions for: 1) in situ annealing of the Al film; 2) controlled cooling rate of the sample; and 3) substrate rotating during deposition. The experimental results show that both substrate temperature and cooling rate after deposition have a major effect on the quality of the Al films. High substrate temperatures will result in rough or island-like Al films, with the formation of grooves or cracks at temperatures above 500 °C, while low substrate temperatures and high cooling rates may result in poor adhesion of the Al film. Both cases can be partly explained by the evolution of the mechanical stresses, including the intrinsic and thermoelastic stresses, in the film-on-substrate system. There are optimal deposition parameters for which the overall stress is minimized. From our experimental results, we found that the optimal temperature lies in the range of 200 °C–400 °C, and the cooling rate is around 10 degree/min. The use of a Ti adhesion layer prevented the peeling off of the Al film from the Si surface during anodization. This is attributed to the difference among the thermal expansion coefficients of Al, Ti, and Si (with values of 25 × 10⁻⁶, 8.5 × 10⁻⁶, and 3 × 10⁻⁶ °C⁻¹, respectively) and to the fact that Ti is chemically less active than Al during anodization, thereby, introduces an effective “shock absorption” in the anodization current change due to the material change when the anodization front reaches the silicon.

After the two-step anodization, the Al layer is completely consumed and turned into a nanopore array alumina film. The total thickness of the deposited Al film is critical to the degree of ordering of the nanopores. A thin Al layer does not allow enough time for the self-organization process to evolve the ordering of the nanopores from their initial random distribution, as shown in Fig. 1(a), to a highly ordered one. We found through the experiments that highly ordered hexagonal pore arrays can be obtained from Al films of thicknesses greater than 40 μm, as shown in Fig. 1(b). The degree of spatial ordering of the pore structures can be clearly assessed in the fast Fourier transform (FFT) images of samples in which concentric rings are seen for the thin Al film Fig. 1(c) and a well-defined sixfold pattern is observed for the AAO from a thick Al film, Fig. 1(d), indicating the hexagonal symmetry with long range order. Fig. 1(e) and (f) show the pore size or CNT diameter distributions for both cases, respectively. It is clear that CNTs grown in an AAO template formed from a thin Al film has a broad diameter distribution and various distorted shapes [Fig. 1(a), (e)], while uniform CNTs, with a narrow size distribution and regular tubular shapes were obtained in the template formed by anodization of a thick Al film [Fig. 1(b), (f)]. It should be mentioned here that, from TEM images (not shown here), CNTs grown from the AAO template are multiwalled and polycrystalline. Improved crystallinity was obtained via high-temperature annealing in vacuum or inert gas atmosphere at 1400 °C–1700 °C; however, some defects remain, which is in accordance with the results from other groups [18], [19].

We note that normally a barrier layer would exist at the bottom of the anodized pores in the Al film after the anodization. This barrier can be removed via continued chemical wet-etching [20] and/or dry-etching (reactive ion etching (RIE) or ion-mill, in case of thin AAO membranes) [21]. Hence, the CNTs grown afterwards could have direct physical contact with the Si substrate, and in effect, may form an electronic heterojunction structure. However, the anodization process exhibited complex behavior when the anodization front approached the interface, with possible Si anodization occurring after the Al film and the Ti buffer layer (if any) were totally anodized. By monitoring the change of the anodization current, one can stop
the anodization at the moment when the silicon interface is reached.

The unprecedented uniformity is not only in diameter and spacing but also in length, which is defined by the thickness of the AAO template which in turn can be altered with the duration of the first anodization step, or if necessary, even with an insertion of an additional anodization. Combination of dry and wet etchings can be used to selectively etch away from the top of the AAO membrane and thereby leave a portion of the nanotubes exposed. Controllably exposing the CNTs from the AAO matrix is achieved with the same process as described earlier [17]. Using the exposed CNT array as a platform for biosensing applications has been demonstrated [22]. With the top tip of the nanotube exposed and its bottom in contact with the silicon, the conductance characteristics of the system can be studied. Again, very rich behaviors can be expected from such a unique system with a heterojunction between two dissimilar materials as well as dimensionalities (three-dimensional to quasi-one-di

mensional) [23] which naturally call for detailed and in-depth investigations which we hope this report will help stimulate in future follow-up studies. It has been shown by multiple groups that laser annealing and high-temperature CVD growth both can improve the crystallinity of CNTs. In this regard, the growth of highly ordered nanotubes on silicon reported here offers the additional advantage over that on an aluminum substrate because it permits a higher growth and/or annealing temperature.

IV. CONCLUSION

In summary, this work demonstrates that highly ordered nanopore arrays of exceptional uniformity can be fabricated directly on silicon substrates by controlled anodization of a thick Al film deposited on a Si substrate under carefully optimized conditions. The anodized aluminum nanopore array film on silicon can then be used as a growth template for CVD growth of CNT arrays of unprecedented uniformity on silicon. This work adds to our tool set a controlled and scalable process for integrating highly ordered CNT arrays onto Si, and enables a wide range of applications in electronics, sensors, displays, and resonators.

REFERENCES


Aijun Yin received the M.Eng. degree and the Ph.D. degree in physical chemistry at the Central South University (formal Central South University of Technology), Changsha, Hunan, China, in 1988 and 1996, respectively. He was a Teaching Assistant and Lecturer in the Department of Chemistry, from 1988 to 1996; an Associate Professor and Deputy Director of the Institute of Physical Chemistry and New Chemical Materials at the Central South University from 1996 to 1999; and a Visiting Scholar at the University of Toronto, Canada, from 1999 to 2000. He is currently a Visiting Professor and Postdoctoral Researcher since 2000 in the Division of Engineering at Brown University, Providence, RI. He has been the lead researcher on the nanofabrication front in supporting most of the lab’s projects as well as multiple cooperations with other groups/labs both in the United States and Canada. His current research interests are fabrication, characterization, and application of nanostructured materials, including carbon nanotubes, nanowires, nanodots, and antidots on various substrates. Dr. Yin is a member of the Electrochemistry Society and the Materials Research Society.
Marian Tzolov received the M.S. degree in physics from Sofia University, Sofia, Bulgaria, and the Ph.D. degree in physics from the Bulgarian Academy of Sciences, Sofia. His doctoral research was on spectroscopy of thin films for solar cells.

He was a Postdoctoral Fellow at Brown University, Providence, RI, where he worked on carbon nanotubes; at the University of Toronto, Canada, working on colloidal quantum dots; and at the University of Bayreuth, Germany, as Alexander von Humboldt fellow working on conjugated polymers. He is currently Assistant Professor at Lock Haven University, Lock Haven, PA. His research is concentrated on photovoltaic, electronic, and optoelectronic applications of organic materials.

Dr. Tzolov is a member of the Materials Research Society.

David A. Cardimona received the B.S. degree in physics and math from Marquette University, Milwaukee, WI in 1976 and the Ph.D. degree in optics from the Institute of Optics, University of Rochester, Rochester, NY, in 1983.

As an undergraduate, he spent a half year at Fermilab helping a team of researchers search for charmed particles. After receiving his advanced degree, he was hired by the Air Force Weapons Laboratory, now the Air Force Research Laboratory, in Albuquerque, NM. As a Theoretical Research Physicist, he has over 20 years of experience in quantum and nonlinear optics, with over 50 papers published in refereed journals and four patents. For the past 14 years, he has performed research in semiconductor heterostructure devices, emphasizing detectors for space applications.

Prof. Xu was awarded eight international and national prizes and awards for his research accomplishments, including the 1995 Steacie Prize of Canada and a 2005 Guggenheim Fellowship. He was editor of IEEE TRANSACTIONS ON ELECTRON DEVICES (1992–1997), on the editorial board of Journal of Physics D, and chaired a number of conferences and committees. He currently serves on the Advisory Boards of several companies and of the National Research Council of Canada.