

Graphitic Structures By Design: Film formation.

By Jonathan Phillips^{1*} and Joe Cordaro²

¹ M.S. E549 , Los Alamos National Lab, Los Alamos, NM 87144

² Materials Research Laboratory, MC5121, University of California , Santa Barbara, CA 93106-5121

ABSTRACT

The potential applications of new graphitic materials, including carbon nanotubes and carbonized spheres, is limited by both the cost of production and the difficulties of organizing them into final geometries. We have developed a simple, low temperature (ca. 500 C) novel technology based on our discovery that in certain lean burn combustion environments graphite will grow rapidly (>1 graphene layer/second) on metallic templates. Post-growth removal of the templates leaves two or three dimensional graphitic structures that mimic the shape of the original graphite. We have created a number of complex structures using this technology including nano graphite particles, macroscopic graphite mesh, and graphite foam. In this study the technique was extended to film formation on silicon. It is intended to be the first step toward the creation of graphitic circuits on the nanoscale.

Introduction

Probably the most exciting potential application for graphitic materials is as a replacement for silicon in the ‘molecular scale’ logic circuit. Indeed, significant energy is directed to the development of carbon nanotubes (1) based circuits. However, the failure to produce any electronic circuit that contains more than a single nanotube highlights a major difficulty: carbon nanotubes cannot be grown in the required complex geometries (2,3). At least for the present they must be grown in one process and organized using a second, and the organizing process remains a significant technological stumbling block.

Given the difficulties organizing nanotubes, researchers are looking for graphite based alternatives to nanotubes. In fact, it is clearly demonstrated that ‘graphene’, that is single basal-plane layers of graphite can be employed as successfully as nanotubes in circuits (4). Thus, there is activity in creating ‘graphene’ via a number of processes including creating SiC in the surface layers of silicon and then decomposing it at elevated temperatures (>1000C) to leave a surface graphite/graphene layer (5). More recently we have demonstrated that Graphene can grow unsupported using an atmospheric pressure plasma torch (6).

In the following we describe current effort to develop another alternative to nanotubes for electronic circuits; Graphitic Structures by Design (GSD). This is a simple technology based on the finding that graphite will grow in multiple layers on the surface of metal templates at relatively low temperatures in certain combustion environments (7). In this paper we report on initial efforts to grow graphite on metallic patterns generated on the surface of silicon wafers.

Experimental

Simple geometric patterns (e.g. 10 micron wide chevron patterns) of Ni were evaporated onto silicon wafers. Samples were made by cutting sections, of the order 5 mm square, from the wafer. Samples were placed in a tube furnace at a specific location, heated to final temperature in argon (460, 512 or 615 C), then exposed to a reducing H₂ (6%)/Ar reducing gas for about 30 minutes. Without changing temperature the reducing gas was then replaced by a flowing mixture of Ar (90%), C₂H₄ (5%) and O₂ (5%) for specified lengths of time ranging from 30 seconds to 30 minutes. Pure argon was then flowed into the system and the samples allowed to cool at a rate of about 20 C/minute. this point and the samples The samples were then examined in an (Hitachi) Scanning Electron Microscope with 90° tilt capability.

Results

Particular attention was given to the impact of temperature, and time on the films formed. Earlier investigations showed that graphite will only form above a certain minimum temperature, that the kinetics of growth are not a strong function of temperature and that growth is linear in time. Although the first two were verified in the present work, the third was not borne out by the present results.

No graphite formed at 460 C, whereas significant graphite was observed at both 512 (Figure 1) and 615 C (Figure 2). The net growth rate at the two temperatures was similar. Perhaps most surprising was that the growth rate was not linear in time. The samples treated for only 30 seconds had less graphite than those grown for 30 minutes, but only by a factor of about two.

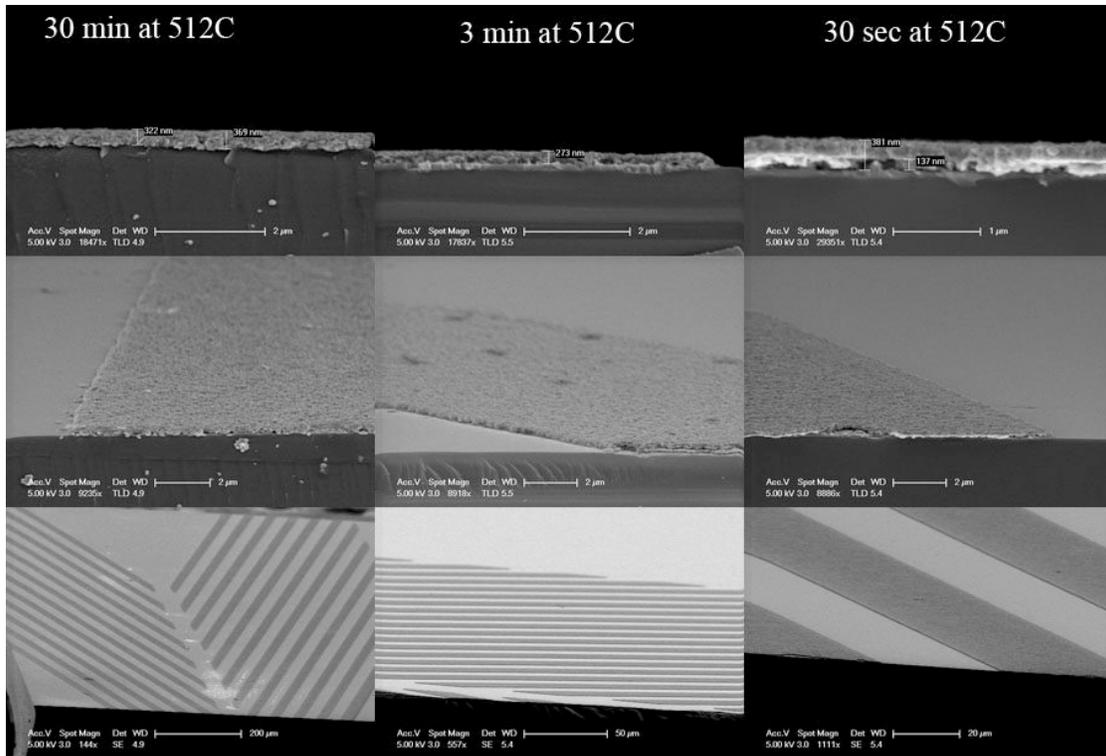


Figure 1- *Films formed at 512 C:* Looking across the top it is clear that the difference in film thickness between a sample generated for 30 second and one grown for 30 minutes is only a factor of two. Other SEM images show that the graphite film follows the template form precisely.

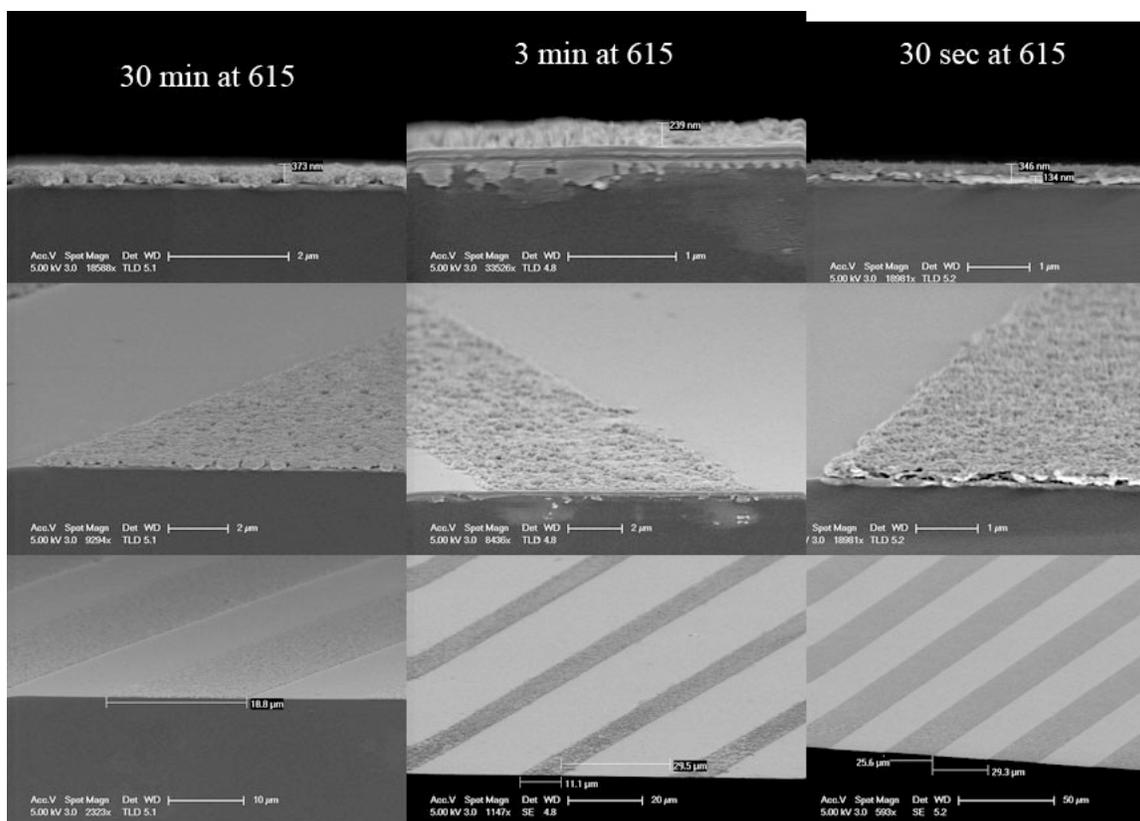


Figure 2- Films formed at 615 C: Looking across the top it is clear that the difference in film thickness between a sample generated for 30 second and one grown for 30 minutes is only a factor of two. It is also clear that all the films created at 615 C are about 40% thicker than those treated for the same length of time at 512 C (Figure 1).

Discussion

This is the most direct demonstration that the GSD approach can lead to the creation of two dimensional graphite ‘designs’ on a silicon substrate. The results suggest a reasonable expectation of similar growth at the nanoscale. Indeed, it is already standard technology to use e-beam techniques to create nano-scale metal patterns. Thus, there will be no limitation on template formation. Although post GSD process removal of the metal template has been demonstrated for ‘free standing’ structures from micro to nano in scale (7), it still needs to be demonstrated for two dimensional graphite arrays.

The present work verifies two earlier findings. Specifically, graphite will rapidly grow to ‘mimic’ the form of nickel metal templates in a fuel rich C_2H_4/O_2 mixture above a minimum temperature (approximately 500C), and that growth rates do not vary strongly over the temperature range at which graphite forms. The failure to observe linear growth kinetics in the film environment of the present work is at variance with earlier work in a ‘packed bed’ environment. Using a Netzche DSC/TGA to study growth on a bed of 200nm Ni particles repeatedly showed linear growth.

In earlier work it was suggested that the mechanism of graphite growth occurs via two mechanisms. At first, the metal template interacts with gas phase radicals formed in the semi-combustion environment of the gas phase to create graphite. Second, once the metal is buried in a layer of graphite, radical precursors hitting the surface are decomposed to release atomic carbon which migrates until it finds a low energy site at the edge of a graphitic plane. It is possible that the present results are consistent with a two step/two rate process. Further investigation is required to determine the source of this discrepancy and to help define the growth mechanism.

REFERENCES

1. Zakhidov, A. A.; Baughman, R. H.; Iqbal, Z.; Cui, C. X.; Khayrullin, I.; Dantas, S. O.; Marti, I.; Ralchenko, V. G., *Science* **282**, 897 (1998).
2. Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A., 'Carbon nanotubes - the route toward applications.' *Science* **297**, 787 (2002).
3. W. Zho, Z. Han, J. Wang, Y. Zhang, Z. Jin, X. Sun, Y. Zhang, C. Yan, and Y. Li 'Cu Catalyzed Growth of SWNT on Substrates', *Nano Lett.* **6**, 2987 (2006)
4. . Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A., 'Electric field effect in atomically thin carbon films'. *Science* **306**, (5696), 666 (2004).
5. Y. Garreau, R. Pinchaux, I. Forbeaux, J.M. Debever, M. Sauvage-Simkin, J.-M. Themlin, Solid State Decomposition of Silicon Carbide for Growing Ultra-Thin Heteroepitaxial Graphite Films, *J. Appl. Phys.* **92**, 2479 (2002).
6. Albert Dato, A. V. Radmilovic, Z. Lee, J. Phillips and M. Frenklach, 'Substrate-Free Synthesis of Graphene Sheets in a Microwave Plasma Reactor', submitted to *Science* April 2007.
7. J. Phillips, M. Nemer, K. Lester, and T. Shiina, 'Graphitic Structures by Design', *Langmuir* **22**, 9694 (2006).