ABSTRACT

Graphitic Structures by Design (GSD) is a novel technology for growing graphite in precise patterns from the nano to the macroscale, rapidly (>1 layer/sec), at low temperatures (ca. 500°C), and in a single step using ordinary laboratory equipment. The GSD process consists of exposing particular metals (Ni, Pd, Pt, Co), which act as ‘templates’, to a fuel rich combustion environment. As an example, we have thoroughly characterized graphite growth on nickel in a mixture of ethylene and oxygen (O₂/C₂H₄ ratio<3), and found that it grows in a geometry remarkably consistent with the shape of the metal template at a rate of the order one graphene layer/second at temperatures between about 500 and 700°C. Graphite structures created with GSD to date include two dimensional ‘screens’ that are inches in extent, yet are composed of micron scale squares graphite foam, hollow nanoparticles, and micron scale particles. All alternative technologies for graphite growth require specialty equipment, such as 2000°C+ ovens, and multiple steps. The alternatives are also not suited for a wide variety of pattern growth in either two or three dimensions. We propose to change focus from demonstrating GSD to determination of the mechanism of graphite growth. GSD could meet a number of recognized technological needs for future generation integrated circuits (IC). Precise patterns of oriented graphite are envisioned as: i) replacements of carbon fibers as structural elements in some aerospace and transport applications, ii) as heat conductive pathways aiding thermal management in ICs iii) as electrical conduits in ICs, iv) as the basic elements of nano-scale logic circuits. GSD graphite is arguably superior to the older and more broadly studied carbon nanotubes technology for all these IC applications for many reasons: only GSD be grown in any pattern on any surface, GSD is far cleaner (no metal residue in the graphite structure, in contrast to nanotubes), GSD structures can be formed consistently and cheaply, at low temperature, and only GSD can be readily grown into large designed macrostructures required for some heat transfer applications.

INTRODUCTION

Graphite is an ‘old’ material, yet surprisingly there are many new ‘high tech’ applications for which graphite in one of its many forms is apparently the best choice. The potential value of new forms of graphite was born out of interest in the new forms it can take, particularly ‘carbon’ (in fact graphite) nanotubes [1]. It is believed that these structures, properly grown and purified, will have unique strength, thermal characteristics and electronic behaviors, and these properties will enable a host of new technologies from space elevators [2] to molecular scale logic circuits [3,4]. Yet nanotubes are simply an elegant nanoscale form of graphite, and most of the ‘special’ properties anticipated for nanotubes can be found in other graphitic structures as well. For this reason designed graphite structures can perform better, or as well as nanotubes in many if not all of technologies suggested for nanotubes. For
example, it is frequently suggested that nanotubes will be the key elements in ‘molecular scale’ logic circuits. Preliminary investigations have validated the feasibility of this concept, yet the necessary purification and then re-organization of nanotubes of the appropriate types into complex two-dimensional networks remains unaccomplished [5].

As a structural material graphite also has a bright future. For example, the newest Boeing airplane (‘Dreamliner’) uses carbon fibers in the primary structural elements because of their high strength to weight ratio. This suggests that graphite will have the strength and weight for a host of aerospace, transport, armor etc. applications. At present the form of graphite garnering the greatest interest from this perspective are carbon nanotubes, woven into macroscopic bodies. However, below we describe a new technology which may be more readily adapted to grow in a single step graphitic objects with high strength to weight ratio.

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 [6]. In this paper we report on initial efforts to grow graphite on metallic patterns generated on the surface of silicon wafers.

EXPERIMENTAL

The apparatus required to grow GSD is simply a tube furnace, operated at atmospheric pressure, and three controlled gas flows (Figure 1). The parameters that have been shown to have the greatest impact on the product are the ratio of gases (ethylene, oxygen and inert), the position of the sample, the total gas flow rate and the temperature. Each of these can have a profound impact on the outcome.

The graphite only grows on proper metal templates. In previous work graphite was shown to grow around a variety of templates including nickel nanoparticles, micron scale nickel lattices, and even graphite foams. In the present work we present data that clearly shows for the first time that ‘2-D’ patterns can be generated on silicon. In one case the pattern consists of a thin layer of titanium and a top layer of nickel. In a second case, films were simply grown on patternless samples, that is metal was sputtered such that it covered the entire silicon substrate.

RESULTS

In Figure 2 we show that under the proper conditions it is possible to generate thin films of graphitic material that precisely mimic the shape of the underlying metal template. This figure also illustrates the sensitivity of the technique to specifics of the process. In this case, the growth dramatically reduced after the first few seconds. In fact, the film thickness after a 30 minute process is barely thicker than an identical sample after 30 seconds of processing. This was found to be a repeatable observation.
Table 1: Results of Raman Spectroscopy

<table>
<thead>
<tr>
<th>Material</th>
<th>G-Peak</th>
<th>D-Peak</th>
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<tbody>
<tr>
<td>Grafoil</td>
<td>1583</td>
<td>1354</td>
</tr>
<tr>
<td>De-Ni, GSD</td>
<td>1583</td>
<td>1353</td>
</tr>
<tr>
<td>Amorphous</td>
<td>1593</td>
<td>1350</td>
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</tbody>
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**KEY:**
- **Grafoil:** Commercial high grade graphite from Union Carbide, Corp.
- **De-Ni GSD:** After Ni particles (200 nm nominal diameter) were treated to the GSD process for 30 minutes, the Ni was removed by acid.
- **Amorphous:** Material made from pyrolyzed sugar.

Initial Raman studies are consistent with the assignment of graphite structure to the films formed on the nickel template (see Table 1). All spectra were taken with 514 nm excitation, 2 mW incident on the sample through a 10x objective. Spectra are the sum of 6 X 10 second integrations (1 minute total). So far only standards and GSD structures grown on Ni particle templates from which the metal has been removed have been studied with Raman. Other techniques [6] also show the material grown on Ni substrates to be graphitic. Precise interpretations of Raman spectra are complicated, but the ‘fingerprint’ interpretation is acceptable [7] to establish that the material is graphitic rather than amorphous.

In contrast to the ‘self limiting’ film formed under one set of conditions, thick films were grown at a steady, rapid rate after relatively minor changes in operating procedure (Figure 3). Approximately 3.5 micron thick films were grown in 30 minutes. This is extremely fast film growth and probably can be improved. No effort was made to optimize it.

The picture suggests the film has other desirable attributes including coherence. That is, the film does break/tear apparently due to compressive stress, yet it is notable that it remains together. Many features of these films will be studied in future work including physical characteristics including moduli, yield stress, thermal conductance, etc.

**DISCUSSION**

Graphitic structures by design technology was employed for the first time to generate precise graphitic 2-D shapes on silicon, suggesting the technique can be mastered to produce a host of structures for integrated circuits including thermal management elements, current carriers and even key elements of logic circuits. It was also shown that the technique must be applied precisely in order to generate large scale, coherent films that grow rapidly (ca. > 0.1 micron/min).

Alternative technologies exist for growing graphitic structures in precise forms, however, these required extremely high temperatures (>2000 C), multiple steps, ceramic substrates, and do not appear readily controllable [7,8].

A great deal of characterization work remains to be done including thermal and electrical conductivity studies, physical property studies and studies of the crystal habit of these films.

**REFERENCES**