Laser Carbon Interactions

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ABSTRACT

Laser processing of materials is not new, but, using lasers to anneal, bond and otherwise transform carbons is. Fundamental understanding of the dependence upon carbon structure, morphology and chemistry is critical to implementing this technology into manufacturing and processing applications. In this work a Q-switched Nd:YAG laser and a continuous wave CO_2 laser are used to anneal carbon materials. Lasers provide rapid heating and cooling with high temporal control. The extent of transformation is kinetically controlled by time above the threshold temperature for transformation. Enabling the production of carbon structures not possible via traditional furnace annealing. The potential technological importance of laser annealing carbon is demonstrated. Examples of material processing and synthesis not possible via traditional furnace annealing are provided. To resolve the nanostructure changes HRTEM is employed.

Keywords: laser annealing carbon, graphitization, carbon nanostructure

1 CONTINUOUS PROCESSING

Perhaps the most over looked application of laser annealing carbon is the ability to do so continuously and rapidly. Graphitization furnaces operate as a batch processing system. Time from start to completion is on the order of a day due to the slow (~25 °C/min) heating rates, long hold times, and slow cooling of the heavily insulated furnace. Additionally, these furnaces require routine maintenance and replacement of expensive speciality graphite heating elements. CO_2 laser annealing provides equivalent material transformation on the order of seconds and modern CO_2 lasers are designed for years of maintenance free use [1]. Although laser annealing is limited to thinner material due to limited heating depth, materials can be annealed continuously and with potentially high throughput. A laser annealed carbon black particle is shown in Figure 1B. The material was heated to 2,600 °C in 1.4 ms under the action CO_2 laser radiation. After annealing for 20 s, the struture is equivalent to that obtained from furnace annealing at 2,600 °C for 1 hr. as has been shown elsewhere [2], thus illustrating the potentially high throughput as the CO_2 laser can operate continously and material is completely annealed in seconds. Higher power lasers and use of multiple lasers can likely anneal bulk materials, uniformly, as well. The CO_2 laser used here is 250 W at maximum power while industrial CO_2 lasers have output powers of tens of kW.

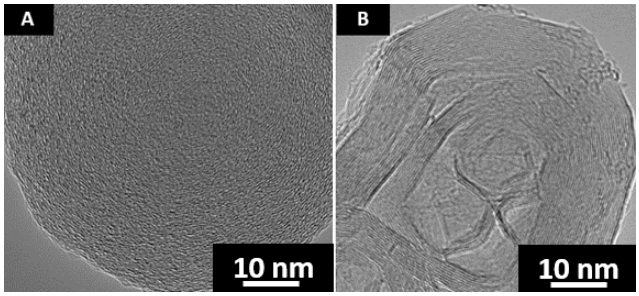

Figure 1. TEM micrographs of A) nascent carbon black and B) carbon black annealed at 2,600°C for 20s by a CO_2 laser.

By temporal control of laser exposure the annealing extent can be controlled for a specific application focus. The power and therefore temperature can also be modified on demand.

2 SURFACE MODIFICATION

The Q-switched Nd:YAG laser pulse width is 8 ns and heats carbon materials to graphitization heat treatment temperatures with a heating rate on the order of a few 10^{11} °C/s. The peak temperature is controlled by the laser pulse energy, typical temperatures range between 2,500 °C to the C_2 sublimation temperature of 4,184 °C [2,3]. The time at elevated temperature is limited (time above 2,000 °C is 1.5 μs). On this time scale, the long range material motions are kinetically restricted. Consequently the Nd:YAG laser annealing trajectory deviates from traditional furnace pathways as shown in Figure 2. The structure in Figure 2 does not approach a furnace equivalent structure with additonal pulses as time above temperature is never long enough given that the particles cool far faster than the repetition rate of the laser (10 Hz) [2].

The limited time at elevated temperature can be used for the purpose of surface modification. Surface modification via kinetically limited oxidation is one potential application.

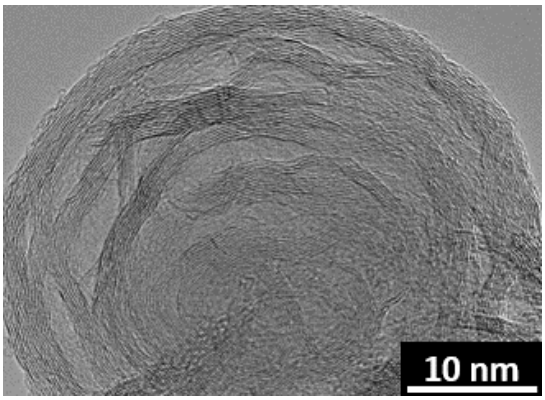

Figure 2. TEM micrograph of carbon black treated with a single Nd:YAG laser pulse of 50 mJ/cm^2 in argon.

For instance, carbon black treated with a single Nd:YAG laser pulse in open air acts to increase the overall particle integrity via annealing the interior while modifying the first several nm of the surface by kinetically limited oxidation. The TEM micrograph in Figure 3 shows that oxidation is limited to the outer surface and the interior of the particles anneals in a similar fashion compared to the particle heated in argon (Figure 2).

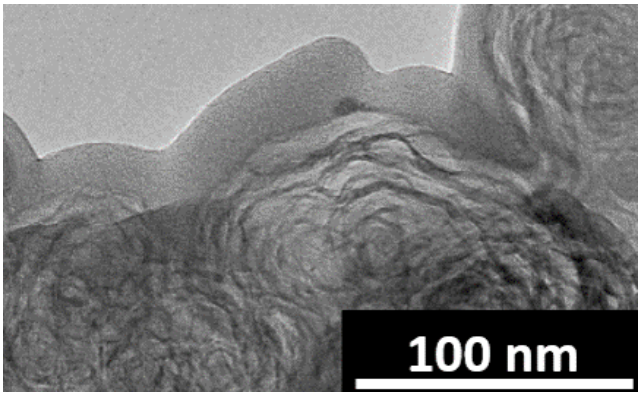

Figure 3. TEM micrograph of cabon black heated with an Nd:YAG laser in open air.

Controlled surface modification via kinetically limited oxidation may potentially be useful for many other materials.

3 THIN FILM ANNEALING

Carbon films serve in a wide range of applications from space craft heat shielding [4] to semiconductor masks [5]. Annealing of such films is limited by the underlying substrate (carbon annealing temperatures exceed substrate melting point). In the case of carbon hard masks that protect semiconductors during processing, the carbon deposition and any post annealing must be under 600 °C so as not to damage the underlying microprocessors. The amorphous carbon films can have high hydrogen content >20 atomic % [6]. Annealing of the amorphous film would make for a more protective mask. However, 600 °C is not high enough to anneal the film in a meaningful way and thus furnace annealing cannot be used. Lasers can be used to anneal just the carbon film and not damage the underlying substrate. As a demonstration, a pyrolytic carbon formed from CVD of ethylene deposited on a Cu substrate was annealed with the CO_2 laser. Details about this material have been previously provided [7]. A SEM micrograph of the unheated pyrolytic film and underlying substrate are shown in Figure 4.

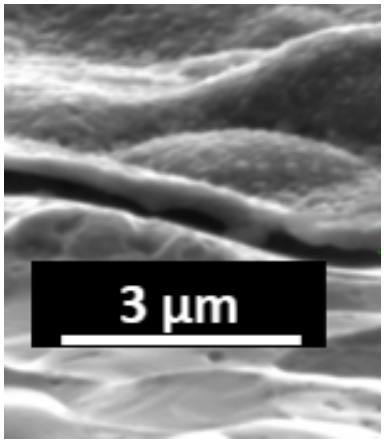

Figure 4. SEM micrograph of the nascent pyrolytic carbon film.

The carbon film is between 200-400 nm thick. After CO_2 laser annealing directly from the top, no apparent changes to the film morphology or underlying Cu substrate were observed in the SEM. The top surface was annealed with 1000 laser pulses, each pulse one ms in duration. The pulses were delayed from one another by 50 ms to provide adequate cooling of the substrate between pulses. The total processing time is less than one minute. Sections of the film were removed from the substrate and crushed in a mortar and pestle both before and after laser annealing for TEM analysis. The films nanostructure before and after annealing are displayed in the TEM micrographs in Figures 5 and 6 respectively.

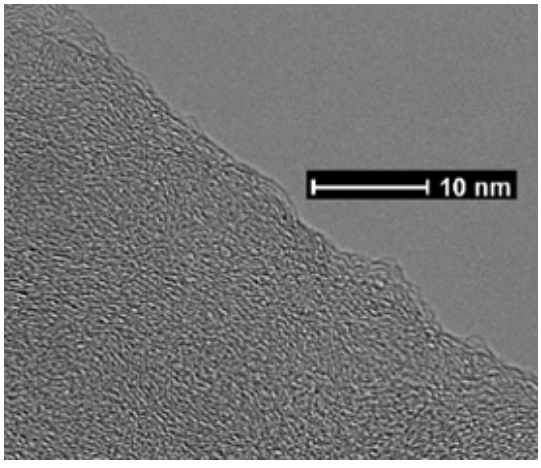

Figure 5. TEM micrograph of as prepared pyrolytic carbon.

As seen in Figure 5 and 6, laser annealing resulted in a significant improvement in material order. The more crystalline laser annealed material will be more resilient and make for an improved carbon hard mask. Laser annealing did not damage the underlying substrate. As carbon film applications continue to increase so too will the potential utility of targeted film annealing via pulsed laser heating.

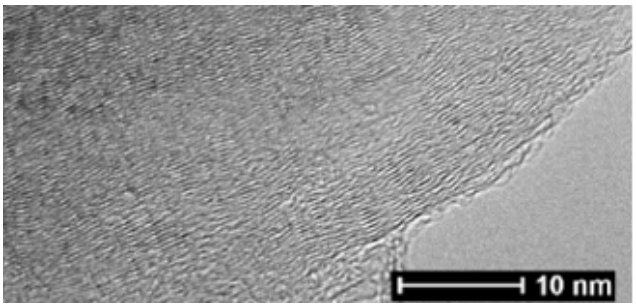

Figure 6. TEM micrograph of pyrolytic carbon treated with pulsed CO_2 laser heating.

4 SELECTIVE LASER SINTERING

During CO_2 laser annealing of carbon black under an argon atmosphere, connecting between aggregates was observed to occur. An illustration of the connections formed is shown in the TEM micrograph in Figure 7.

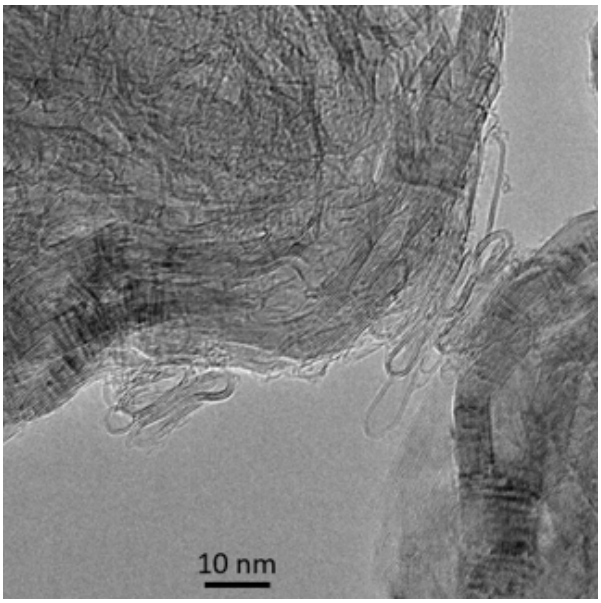

Figure 7. TEM micrograph of laser sintered carbon black.

The connection shown in Figure 7 has an ordered structure and thus is unlikely a result of solidified carbon vapor. The connection appears to be the result of a singular layer partially detaching from the particle and connecting to the neighbor. This type of connection was common when annealing with high energy 100 µs CO_2 laser pulses (16.4 J/cm^2). Further connections of this type are highlighted in the TEM micrograph in Figure 8.

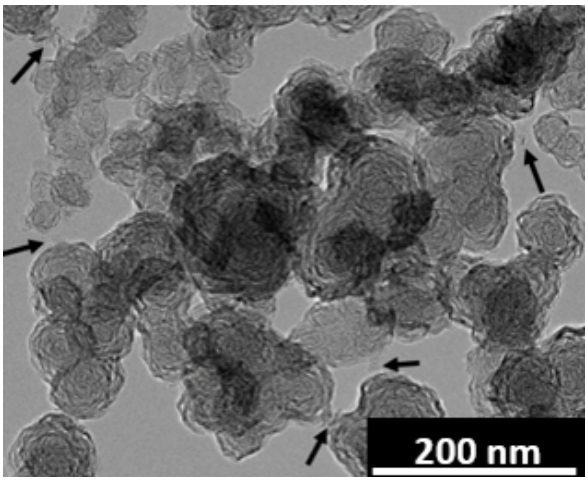

Figure 8. TEM micrograph of laser sintered carbon black.

The product material is believed to have increased electrical conductivity based on the observed structure. The connections may provide long range electrical conductivity as compared to the starting carbon black. These connections were made without additional material. Laser sintering a mixture of materials could result in a wide range of potential applications.

5 FROZEN INTERMEDIATE STRUCTURES

Heat-Treatment-Temperature (HTT) and resulting carbon structural transformation has been extensively studied. A detailed quantification of HTT and resulting material annealing was provided by Oberlin in 1984 [8]. The four stages outlined in Oberlin's HTT diagram (temperature dependent) are believed to be separated by "very rapid" transitions [8]. So rapid, in fact, that intermediate structures are not observable on furnace heating timescales (several minutes minimum) due to slow ramp rates and have thus been ignored. These intermediate structures remain unexplored and represent an entirely new class of carbon materials. It has been demonstrated that CO_2 laser heating results in equivalent end structure as compared to furnace annealing [1]. The high temporal control of CO_2 laser annealing allows for exploration of such intermediate structures that can be captured by the rapid heating and cooling timescales.

Sucrose char for instance is one such material that passes through a unique intermediate structure. Sucrose char lamellae have an arduous path towards restructuring due to the curvature and intertwined nature of the lamellae in sucrose char as is common for non-graphitizable carbons.

The pathway towards final annealed product is highlighted in the TEM micrographs shown in Figures 9-11. Sucrose char was prepared by carbonization at 500 °C for 5 hrs.

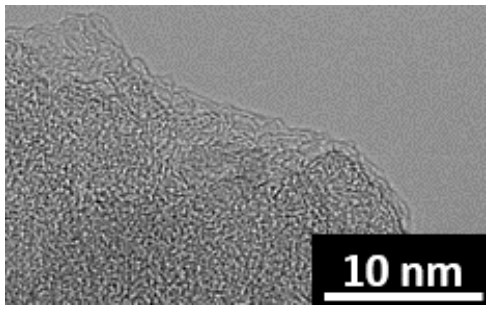

Figure 9. TEM micrograph of as prepared sucrose char.

The nanostructure of sucrose char after 5 seconds of isothermal annealing at 2,600 °C is comprised almost entirely of quasi-spherical closed shell particles as shown in Figure 10.

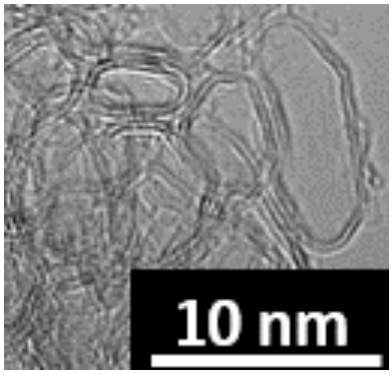

Figure 10. TEM micrograph of sucrose char after 5 s laser treatment at 2,600 °C.

The end structure obtained after annealing for 30 seconds is equivalent to traditional furnace heating at 2,600 °C for a duration of 1 hr [1].

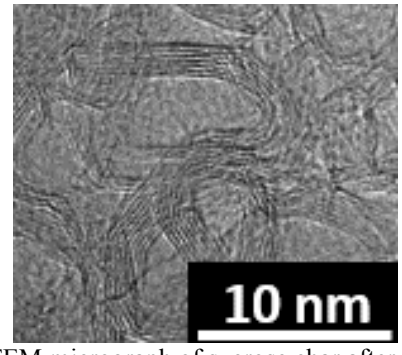

Figure 11. TEM micrograph of sucrose char after 30 s laser treatment at 2,600 °C.

Therefore, CO_2 laser annealing with a heating rate of 1.84 x 10^6 °C/s is equivalent to traditional annealing for this material. Considering the final annealed products are equivalent, the trajectories observed here during short pulse durations are also likely occurring in traditional furnace heating, yet are undetectable due to the limited temporal control. The end structure is cage-like and no longer consists of the closed shell particles as found after 5 s of laser annealing. This frozen intermediate structure highlights the potential of contolled laser heating.

CONCLUSIONS

A few potential applications of laser carbon material processing have been illustrated. Applications presented here are those that cannot be performed by traditional furnace annealing. This is far from an exhaustive list and lasers are poised to be instrumental in the advancement of carbon science and technology.

REFERENCES

[1] J.P. Abrahamson, Pulsed laser annealing of carbon, Ph.D. Thesis, Penn State, 2017.

[2] J.P. Abrahamson, M. Singh, J.P. Mathews, R.L. Vander Wal, Pulsed laser annealing of carbon black, Carbon 124 (2017) 380–390. doi:10.1016/j.carbon.2017.08.080.

[3] H.A. Michelsen, C. Schulz, G.J. Smallwood, S. Will, Laser-induced incandescence: Particulate diagnostics for combustion, atmospheric, and industrial applications, Prog. Energy Combust. Sci. 51 (2015) 2–48. doi:10.1016/j.pecs.2015.07.001.

[4] O. Feron, F. Langlais, R. Naslain, J. Thebault, On kinetic and microstructural transitions in the CVD of pyrocarbon from propane, Carbon 37 (1999) 1343–1353. doi:10.1016/S0008-6223(98)00329-7.

[5] S. Lee, J. Won, J. Choi, S. Jang, Y. Jee, H. Lee, D. Byun, Preparation and analysis of amorphous carbon films deposited from (C6H12)/Ar/He chemistry for application as the dry etch hard mask in the semiconductor manufacturing process, Thin Solid Films. 519 (2011) 6737–6740. doi:10.1016/j.tsf.2011.01.405.

[6] T. Lee, N.-K. Min, H.W. Lee, J. Jang, D. Lee, M. Hong, K.-H. Kwon, The deposition of amorphous carbon thin films for hard mask applications by reactive particle beam assisted sputtering process, Thin Solid Films. 517 (2009) 3999–4002. doi:10.1016/j.tsf.2009.01.112.

[7] P. Gokulakrishnan, R. Joklik, C. Fuller, R. Vander Wal, J. Abrahamson, Experimental and modeling investigation of pyrolytic carbon deposition relevant to fuel film cooling in rocket engines, in: 55th AIAA Aerosp. Sci. Meet., The American Institute of Aeronautics and Astronautics, Grapevine Texas, 2017. doi:10.2514/6.2017-1787.

[8] A. Oberlin, Carbonization and graphitization, Carbon 22 (1984) 521–541. doi:10.1016/0008-6223(84)90086-1.