Journal of Physics and Chemistry of Solids 75 (2014) 1029–1032

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Field-effect switching in nano-graphite films

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ARTICLE INFO

Article history:
Received 2 November 2013
Received in revised form
26 February 2014
Accepted 18 March 2014
Available online 5 May 2014

Keywords:
A. Thin films

ABSTRACT

The effect of electrical resistivity switching in nano-graphite films is described. In difference with cases published elsewhere the switching in nano-graphite films occurs from stable high conductive to metastable low conductive state. Critical current of switching varies in the range 10–500 mA and is believed to increase up to values of 100–1000 A appropriate for using of nano-graphite samples in power grids as contact-less current limiters and circuit breakers. The possible mechanisms of switching phenomenon in nano-graphite films are discussed.

Physical and electromagnetic properties of carbon and its derivatives are the subjects of constant interest and extensive studies for many years. Attention has been paid to the switching behavior in the carbon graphite like materials. Antonowicz more than 30 years ago investigated the conductive properties of the glassy carbon [1] and its evaporated deposits [2] and has found out the effect of jump of conductivity up to three orders of magnitude. The change of conductivity was reversible, and the relaxation time made some days.

Jang and Zhao also studied the switching behavior of carbonized materials [3]. They studied the partially carbonized polyacrylnitride fibbers, which were observed to undergo a resistivity change between 2 and 4 orders of magnitude at a transition temperature typically in the range of 98–200 °C. The current–voltage curves exhibited an initial supercurrent-like increase, followed by a rapid drop to a high resistance state, and then a rise in current again at a later stage.

Goldberg et al. have obtained the US patent on the carbon switching device [4]. This device was made on the base of partially pyrolyzing polymer material by heating the material between 500 °C and 800 °C. Electrodes are connected with the material at two different locations to produce an electrically active element therebetween. Devices made according to the teachings of the disclosure exhibit negative resistance in a part of their voltage–current characteristic and run as the bi-directional electronic switches.

The author of this paper spent more than twenty years for study of the thin carbon films having in mind their application first as the strippers for the charge particle beams. Later on attention has been paid to the electromagnetic properties of thin carbon films. Some anomalies in the electromagnetics of the films formed by sputtering of spectroscopic pure graphite in electrical arc discharge and also by chemical vapor deposition (CVD) methods have been found [5–8]. This was the field effect electrical resistivity jump, which can be used for current limiting in electric circuits and smart chips, the *rf*-to-*dc* conversion and the optical radiation emitted after switching off, which can be utilized in various optoelectronic devices.

In this letter we report about switching behavior observed in NG films, which can be used potentially as current limiters in smart grids.

The nano-graphite films used in these experiments were obtained by means of CVD method on the quartz substrate. The CVD process has taken place in thermal activated isobutanol with a pressure of about 0.1 atm at the temperature of 900 °C. As a result the 0.1–1 μm thick NG film has been produced in 3–15 min. Fig. 1 represents typical scanning electron microscopy (SEM) image of NG film. As can be seen at the highest magnification of 20,000 the surface of deposited film looks structureless which means that the film is amorphous. This result is consistent with the representation [9] about NG films as a composite of small graphite-like sp^2-bonding granules embedded in the matrix of amorphous carbon. This conclusion is supported by in-situ Raman spectroscopy.

The typical Raman spectrum of NG film is shown in Fig. 2. In this spectrum Raman D-band at 1360 cm^{-1} and G-band in the vicinity of 1600 cm^{-1} are specific for different forms of disordered graphite. The height equality of D and G peaks corresponds to graphite crystalline size of the order 20–30 A [10].

The presence of D peaks is the indicator of sp^2 clustering. The D peak arises due to the breathing modes of sp^2 atoms in aromatic rings. Its intensity is strictly connected to the presence of sixfold

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http://dx.doi.org/10.1016/j.jpcs.2014.03.016
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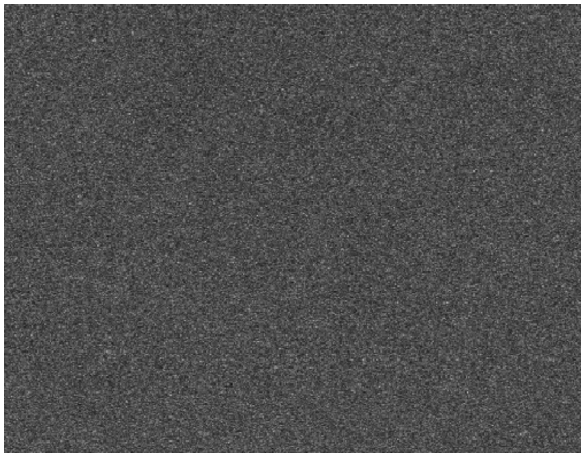

Fig. 1. SEM image of typical nano-graphite film with the magnification of 20,000.

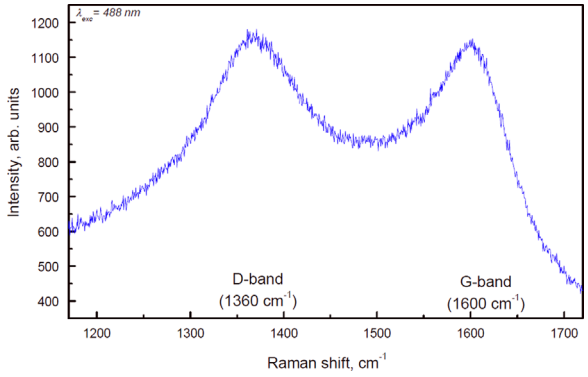

Fig. 2. Raman spectrum of typical nano-graphite film. G and D-bands attributed to different forms of disordered graphite are clearly seen.

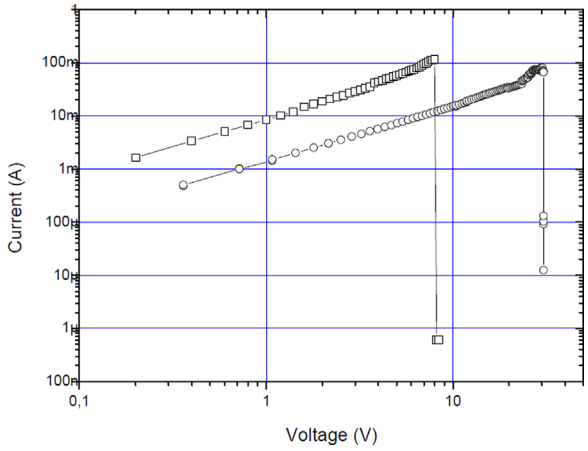

Fig. 3. Room temperature *I–V* characteristics of 1 μm layer of NG film on quartz substrate. Squares and circles depict manual and computer current control respectively. Four to five orders of magnitude resistivity jumps at critical current of 100 mA are easily seen.

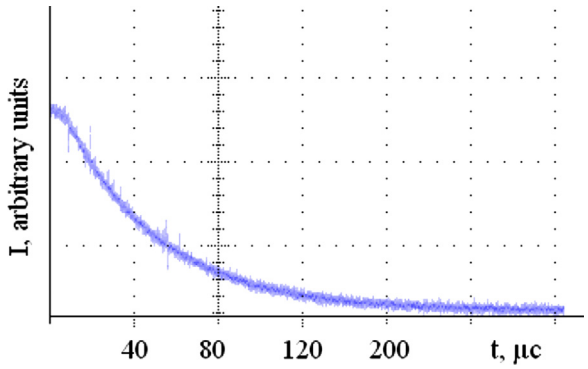

Fig. 4. Switching rate of nano-graphite film sample. Measurement of current decay was made at ballast resistance in the vicinity of critical current in Fig. 3.

rings. Tuinstra and Koenig [11] noted that the ratio of its intensity to that of the G peak varied inversely with L_a – the cluster diameter or in-plane correlation length:

$$I(D)/I(G) = C(\lambda)/L_a, \quad (1)$$

where $C(515.5\ \text{nm}) \sim 44$ Å. So the cluster size is unequivocally defined by the above relation. Moreover, the position of G peak at 1600 cm^{-1} is the evidence of nanocrystalline graphite [12].

For the conductive measurements we used the samples of 1–2 cm^2 square with copper current leads arranged in planar geometry and connected to film surface by means of a silver paste. *I–V* and switching characteristics of these samples were studied using both LabVIEW and manual controlling current source.

The current–voltage and electrical switching characteristics of NG film samples at room temperature are shown in Fig. 3. In the "ON" state with the increasing voltage the current through the sample initially increase linearly (Fig. 3). Near the critical current the samples show nonlinearity. At the critical current the samples exhibited jump into "OFF" state with the resistivity four to five order of magnitude higher than that into the "ON" state. Such a resistivity jump looks like metal–insulator transition. The value of critical current varies in the range 0.01–0.5 A. This value is limited by difference in thermal expansion of NG film and substrate.

It is believed that the increase of critical current of NG film up to commercial interesting value of 100–1000 A is possible to be used as contactless current limiters and circuit breakers for power grids.

When the applied voltage decreases to zero the sample reverts into the "ON" state and the switcher can be used repeatedly many times. As can be seen from Fig. 3 the change of resistivity up to four to five orders of magnitude occurred as a result of switching.

The switching rate measurement has been made by oscilloscope on load resistance. The switching process is shown in Fig. 4. As can be seen the duration of switching process is about 200 μs. This value varies up to 50% from sample to sample.

Such switching behavior is drastically different from other switchers described elsewhere [13–15]. The essential of all of these devices is switching from the low conducting (LC) to high conducting (HC) state. For explanation of such kind of switching numerous hypotheses has been proposed: thermal and double injection mechanism [16], exciton's mechanism [13] and bistability caused by the overheating of electrons [17–20].

Thermal mechanism fails to explain our results due to fast switching with "electronic" time of 100–200 μs (see Fig. 4). Also we observed optical radiation emitted few milliseconds after switching off [7]. It is believed this process is related with thermo-cooling of sample after switching.

Double injection mechanism suggests the existence of trap centers in the structure. Saturation of these centers with injected curriers gives rise to jump into LC state. However it is not possible to reverse this process to produce LC to HC transition.

As for the hypothesis of hot electrons the steep change of resistivity on few orders of magnitude should be located in near vicinity of working temperature. In the case described in [17,18] this is the superconductor–insulator transition near the critical temperature. In Ref. [3] the evidence of steep metal–semiconductor transition between HC and LC around a temperature of 425 K is