



Full Length Article

Water enrichment/depletion of amorphous carbon coatings probed by temperature-dependent dc electrical conductivity and Raman scattering

Svetlana V. Saparina^a, Alexandr I. Fishman^a, Andrei A. Stolov^b, Jie Li^b, Sergey S. Kharintsev^{a,*}

^a Department of Optics and Nanophotonics, Institute of Physics, Kazan Federal University, Kremlevskaya, 16, Kazan 420008, Russia

^b OFS, 55 Darling Drive, Avon, CT 06001, USA

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ABSTRACT

Amorphous carbon (a-C) is an appealing disordered multi-phase material widely used as a cost-effective barrier coating (10–100 nm thick) for silica optical fibers to protect them from harsh environments. Those coatings prevent strength degradation of the optical fibers by moisture and, also block hydrogen diffusion into the fiber. In this paper, we experimentally study the *in situ* temperature-dependent dc electrical conductivity and Raman scattering of dried/wetted a-C coatings under multiple heating/cooling cycles within the range of 40–120 °C. At temperatures of above 80 °C, we observe hysteresis in both the dc electrical resistance and the Raman scattering intensity. One of the mechanisms is related to the escape of intercalated (or spatially confined) water from the a-C coating, causing the resistance decrease due to a closing of the bandgap. The opposite is observed when some water molecules experience dissociative absorption at the edge and basal defects that may be decorated with C–H, COOH/C–OH and C–O–C/C=O functional groups. The content of water within the a-C coating is quantified through relative contributions of the water and edge defect related Raman bands. This study expands our knowledge about a-C ultrathin films, originally designed as barrier coatings, towards promising ultracompact humidity sensors and next-generation adsorbents.

1. Introduction

Amorphous carbon (a-C), compared to a pristine graphene or even its defective counterpart (graphene oxide), represents a highly disordered carbonaceous material containing a huge amount of structural defects and dopants (of the order of 10^{17} – 10^{20} cm⁻³) [1]. It is well known that the defects such as edges, vacancy sites and boundaries may affect electronic properties of disordered quasi-graphite crystallites. For example, defects can lead to the opening of the band gap which impacts the performance of carbon-containing electrical components [2–5]. A high concentration of defects plays a negative role – it impedes the electron/hole mobility and essentially deteriorates the material conductivity. On the other hand, doping provides a way to directly control the electronic features of a-C coatings through substitution of carbon atoms with adsorbed molecules of gas and liquid that operate as donors/acceptors [6]. Chemical functionalization enables changing the Fermi level [7] and opening the band gap in quasi-graphite crystals in a tunable and reversible way [8]. Due to its imperfect structure, containing defect-rich sp²/sp³ crystallites, a-C coatings react more easily with intercalated water under mild annealing. The H₂O molecules near

the edge defects are capable of chemical dissociation into H⁺ and OH⁻ with further formation of functional entities such as COOH/C–OH, C–O–C/C=O and C–H, breaking the energy barrier of 0.7 eV at ambient conditions [9]. Importantly, defective sites on a basal plane are less chemically reactive compared to the edge defects [10] and, are therefore negligible. Amorphization of carbon alleviates water dissociative absorption.

Raman spectroscopy is one of the valuable spectroscopic probes for characterizing defects and dopants in carbonaceous materials. However, the interpretation of Raman spectra of a-C is still not a trivial task because specific Raman bands clump together within the spectral range of 1000–2000 cm⁻¹ (here we will not deal with the second-order Raman bands at around 2700 cm⁻¹) [11–13]. For this purpose, a multi-peak fitting analysis is widely used to decompose a broad Raman spectrum into four [14,15], five [16–18], six [13] or even seven [19,20] elementary peaks. In our study, we utilized a regularized least-squares method, in which additional *a priori* information on sought solutions such as the lineshape and non-negativity was used.

It is well established that all carbonaceous materials reveal a G band at around 1580 cm⁻¹ which is attributed to a doubly-degenerate (TO

* Corresponding author.

E-mail address: Sergey.Kharintsev@kpfu.ru (S.S. Kharintsev).