Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 254 (2007) 55–61
applied surface science
www.elsevier.com/locate/apsusc

Origin of localized states in graphite: Indirect photoemission processes or impurities?

M.E. Dávila [a,*], M.A. Valbuena [a], V. Pantín [a], J. Avila [b], P. Esquinazi [c], M.C. Asensio [b]

[a] *Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas (CSIC), C/ Sor Juana Inés de la Cruz, 3, 28049 Madrid, Spain*
[b] *Synchrotron SOLEIL, Orme des Merisiers, Saint Aubin BP 48, 91192 Gif sur Yvette Cedex, France*
[c] *Department of Superconductivity and Magnetism, Leipzig University, Germany*

Available online 20 July 2007

Abstract

The electronic band structure of different types of graphite samples have been investigated in order to identify the origin of non-dispersive density of states recently reported in the literature. A systematic series of synchrotron radiation angle resolved photoemission spectroscopy (ARPES) measurements on graphite single crystal, highly oriented graphite (HOPG) and epitaxial grown graphite single crystal on 6H–SiC(0 0 0 1) samples, have been carried out as well as compared with theoretical tight binding calculations. Our results indicate that these localized states are present in all the graphite-investigated samples showing the same non-dispersive character and at the same binding energies. The photoemission data taken at several photon energies demonstrate that these states are not surface states nor due to indirect photoemission processes. It seems that they are closely related to the level of impurities present in the studied samples.

PACS : 71.20.b; 71.23.k

Keywords: Photoelectron spectroscopies; Electronic structure; Low-dimensional solids; Graphite

1. Introduction

The interest on graphite has been renewed due to the unexpected properties (magnetic, transport, etc.) [1–4] recently reported of new allotropic carbon forms [5,6], i.e. nanotubes, foams, which have been evidenced thanks to the development of advanced techniques allowing the visualization of novel exotic properties, unknown until now. In fact, recent PES and STS/STM studies on graphite-based systems have reported a particular signature characterized by the presence of localized state near E_F in the density of states (DOS) [7–10]. These peculiar electronic states have been related to a wide variety of magnetic or transport properties [11,12] of graphite materials, which are still not fully understood.

As we have recently indicated, HOPG samples show dramatic decrease in their conductivity as a function of the level of defects and order in the investigated materials [7]. The better ordered HOPG samples displayed a metallic behaviour, while poorly ordered samples exhibited a semiconductor character. Magnetic measurements have also showed a probable ferromagnetism and/or superconducting-like behaviour in HOPG depending on the existence of topological defects observed in the investigated samples [13]. This subject has been initially investigated by Lanzara's group [14], followed by many others [15–17].

To better understand the origin of such anomalous properties, a large set of different graphite samples have been systematically investigated by ARPES. The valence band electronic structure of metallic and semiconductor HOPG graphite samples, graphite single crystals as well as epitaxial graphite single crystals grown on SiC(0 0 0 1) substrates have been measured and compared with tight binding theoretical calculations.

This paper is organized as follows. In Section 2 the experimental details are given. In Section 3 our results and discussion are presented and Section 4 summarizes our conclusions.

* Corresponding author.
E-mail address: mdavila@icmm.csic.es (M.E. Dávila).

0169-4332/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2007.07.119

2. Experiment

The photoemission measurements were performed at the ANTARES experimental station of the SU8 beamline at the LURE-SOLEIL synchrotron radiation laboratory, where a PGM-VLS monochromator provides photons in the wide energy range from 15 to 950 eV. Linearly polarized monochromatic light was used with an incident angle of 45° and the electric vector lying in the plane of incidence containing the surface normal. We have used photon energies ($h\nu$) of 73 and 30 eV in the experiment, with a typical energy resolution of 50 meV. The UHV chamber was equipped with a 50 mm hemispherical VSW angle-resolving analyser mounted on a two-axis manipulator with an overall angular resolution of 0.5°. The basic pressure during the measurements was always lower than 1×10^{-10} Torr. Alternatively, two types of graphite HOPG samples, type I (metallic character) and type II (semiconductor character) were used to determine the electronic structure at different photon energy and polarization. All single-crystal samples have been well studied together with epitaxial thick films of graphite single crystals grown on SiC substrates.

The HOPG investigated samples were obtained from two different sources the Research Institute 'Graphite' (Moscow) [7,17] and from Advanced Ceramics (USA) [7]. The typical size of the samples was 3 mm × 3 mm. They were structurally characterized by X-ray diffraction and the magnetic and transport properties were carefully measured [13]. Our HOPG samples were synthesized by deposition of carbon materials from the gas phase at temperatures about 2000 °C onto a heated material followed by heat treatment under pressure at about 3000 °C. The quasi-single crystal prepared in this manner, formed by many single crystals, has a structure constituted by different domains, which have random orientation in the basal plane. The *c*-axes of small graphite crystallites are parallel to each other and perpendicular to the surface of the film, while the directions of the *x*- and *y*-axis are distributed arbitrarily. The clean HOPG samples revealed a LEED pattern formed by rings instead of spots, which is consistent with samples comprising a large number of micron-size crystallites and that present random in-plane orientations. The obtained pattern corresponds to an incoherent superposition of many single-crystal diffraction patterns. It also means that any off-normal photoemission spectrum measured on these samples is the result of the integrated photoelectrons emitted over a statistical distribution of disoriented crystals along the azimuthal angle.

On the other hand, flakes of graphite single crystal with surface areas of typically 5 mm × 5 mm were studied. They could be cleaved in situ with a tape, the clean graphite single-crystal surfaces revealed a hexagonal LEED pattern instead of the rings signalled above.

The last graphite sample studied was prepared by thermal epitaxial growth on the Si-terminated surface of 6H–SiC(0 0 0 1). The substrate was cut from a commercial 0.3-mm-thick nitrogen doped 6H–SiC wafer (CREE Research). It was fixed on a hollow Mo sample holder with an electron bombardment heating system on the underside. After introduction into the ultrahigh-vacuum chamber, the sample was heated to 850 °C under a Si flux from a resistively heated Si wafer. This cleaning procedure, which removes the native surface oxide, leads to a Si-rich 3 × 3 reconstruction as observed by LEED. The sample was then annealed for several minutes at

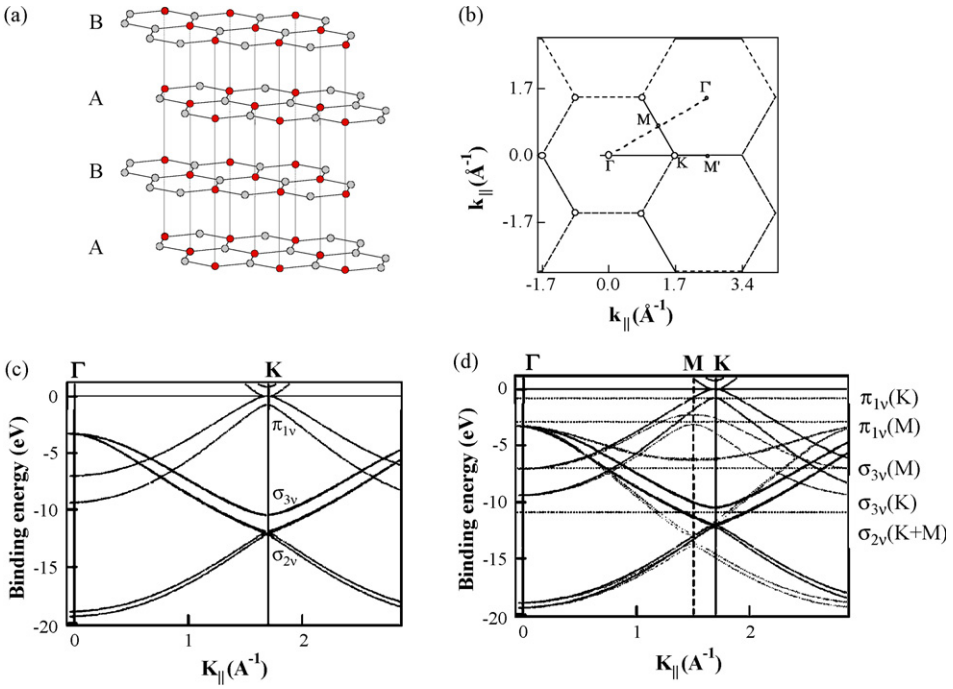

Fig. 1. Panel (a) shows schematically the graphite 3D atomic structure; in panel (b) the 2D first Brillouin zone (BZ) along with the neighbouring BZ ones. In (c) we can see the calculated 2D graphite band structure along ΓK symmetry direction and panel (d) shows together the theoretical bands ΓK and ΓM. This panel helps to understand the electronic band structure in HOPG samples.