

Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



Volume 254, No. 1, 31 October 2007 ISSN 0169-4332

# applied surface science

A journal devoted to applied physics  
and chemistry of surfaces and interfaces

Proceedings of the 13th International  
Conference on Solid Films and Surfaces

San Carlos de Bariloche, Argentina,  
6th–10th November 2006

Guest Editors:

Guillermo Zampieri, Esteban A. Sánchez, Mónica Guraya,  
María C. Asensio, Hugo Ascolani

Volume 254, No. 1, pp. 1–424

31 October 2007

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect  
<http://www.elsevier.com/locate/apsusc>

This article was published in an Elsevier journal. The attached copy is furnished to the author for non-commercial research and education use, including for instruction at the author's institution, sharing with colleagues and providing to institution administration.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



# Experimental and theoretical study of charge transfer in hydrogen ion scattering from a graphite surface

F. Bonetto<sup>a,\*</sup>, E.A. García<sup>a</sup>, R. Vidal<sup>a,b</sup>, J. Ferrón<sup>a,c</sup>, E.C. Goldberg<sup>a,c</sup>

<sup>a</sup> Instituto de Desarrollo Tecnológico para la Industria Química (INTEC-CONICET), Güemes 3450, 3000 Santa Fe, Argentina

<sup>b</sup> Universidad Católica de Santa Fe, Santa Fe, Argentina

<sup>c</sup> Fac. de Ingeniería Química, Universidad Nacional del Litoral, Santa Fe, Argentina

Available online 10 July 2007

## Abstract

Ion scattering spectrometry (ISS) with time of flight (TOF) analysis is employed to measure the ion fraction of positively charged hydrogen ( $H^+$ ) projectiles scattered from a well characterized highly oriented pyrolytic graphite (HOPG) surface at a  $45^\circ$  scattering angle, various ingoing/outgoing angles and two different incoming energies (4 and 5 keV). In the theoretical approach, the negative ionization probability is calculated by employing a Green's function formalism to solve the dynamic collisional process. Both theoretical and experimental results are analyzed and contrasted. The theoretical negative ion fraction evolution during the collisional process is described in detail.

© 2007 Elsevier B.V. All rights reserved.

PACS : 68.49.-h; 34.70.+e; 81.05.Uw

Keywords: Charge transfer; Graphite surface; Hydrogen scattering

## 1. Introduction

The ISS technique is capable to discriminate contributions to the backscattering yield coming from both different atomic layers and different atoms present in the surface. The collision process is a dynamical situation in which charge exchange between the projectile and the solid target evolves in time. Neutralization of scattered ions is strongly dependent on the system projectile-target system [1].

Measurements of positive and negative ion fractions backscattered at  $135^\circ$  from nonmetallic surfaces, have been performed for hydrogen and deuterium ions incident with energies in the range 3–20 keV [2]. High negative ion fractions observed for 400 eV hydrogenous ions ( $H^+$ ,  $H_2^+$ ,  $H_3^+$ ) incident on polycrystalline graphite [3], are not observed from clean HOPG [4]. Tsumori et al. [3] found that the negative yield obtained on a polycrystalline graphite surface is comparable to that found on low work function surfaces, e.g., Cs or Ba-covered surfaces with work functions between 1.9 and 2.5 eV.

However, the work function of graphite is about 5 eV. This means that conventional charge transfer theories [5] cannot explain the high  $H^-$  ion fraction.

Another point to be taken into account is the density of states (DOS) for graphite. HOPG has a region with very low DOS near the Fermi level. This region may act like the band gap in semimetals. In view of the results obtained for Si [6]; the low HOPG DOS at the Fermi edge is expected to strongly influence the  $H^-$  survival probability while the ion is close to the surface.

## 2. Experimental

The experiments were carried out in an ultra-high-vacuum (UHV) chamber. Ions and neutrals scattered off the graphite surface were detected by the TOF technique [7]. The ions were produced in a discharge source and mass-analyzed using a Wien filter. Neutrals plus ions scattered at a fixed angle of  $45^\circ$  are detected at the end of a drift tube by a channeltron electron multiplier. To separate the ions from the neutrals, after scattering from the graphite surface, a pair of deflection plates placed at the drift tube entrance was used. The HOPG sample was mounted on a manipulator that allows changing the incident and exit angles. The sample was cleaved in air and

\* Corresponding author at: INTEC-CONICET, Güemes 3450, S3000GLN Santa Fe, Argentina. Tel.: +54 342 4559174.

E-mail address: [bonetto@ceride.gov.ar](mailto:bonetto@ceride.gov.ar) (F. Bonetto).

cleaned by annealing at 1000 °C by electron bombardment of the sample holder.

### 3. Theory

The present formalism used to describe the charge transfer in  $H^+$  scattering from a HOPG graphite surface is based on the assumption of rapid neutralization of  $H^+$  colliding particles due to a very efficient resonant mechanism. Then, the  $H^-$  formation from neutral atoms provides a good approximation to the  $H^+$ /graphite collision.

The interaction between the colliding projectile and the surface involves the substrate atoms inside a sphere of 12 bohr radius centered at the projectile position at each point of its trajectory. The incoming and outgoing trajectories of the projectile are roughly simulated by two broken straight lines with proper incidence and exit angles.

The Anderson–Newns Hamiltonian in the spin-less approximation is given by:

$$H(t) = \sum_k \varepsilon_k \hat{n}_k + \sum_c \varepsilon_c \hat{n}_c + E_a(t) \hat{n}_a + \sum_k [V_{ak}(t) \hat{c}_a^\dagger \hat{c}_k + \text{h.c.}] + \sum_c [V_{ac}(t) \hat{c}_a^\dagger \hat{c}_c + \text{h.c.}],$$

where index  $a$  refers to the active state of the projectile atom with energy  $E_a(t)$ ; and  $k$  and  $c$  indexes point out the valence and core surface states respectively, with energies  $\varepsilon_k$  and  $\varepsilon_c$ , respectively.  $V_{ak}(t)$  and  $V_{ac}(t)$  are the respective projectile–surface hopping terms.

The corresponding occupation operators are defined in terms of the creation and annihilation operators as  $\hat{n}_k = \hat{c}_k^\dagger \hat{c}_k$ ,  $\hat{n}_a = \hat{c}_a^\dagger \hat{c}_a$ . The average value  $\langle \hat{n}_a(t) \rangle$  gives the probability that the projectile state is occupied at the time  $t$ . This value can be obtained from the Green function:

$$F_{aa}(t, t') = i \langle c_a^\dagger(t') c_a(t) - c_a(t) c_a^\dagger(t') \rangle, \quad \text{for } t = t', \quad \langle n_a(t) \rangle = \frac{1}{2} [1 - i F_{aa}(t, t)],$$

This Green function and the advanced one,  $G_{aa}(t, t')$ , are necessary to solve the problem. The self-energies determining the Green functions motion equations depend on the local HOPG DOS and the atomic H–C hopping integrals.

### 4. Results and discussion

The TOF spectra for total (neutrals plus ions) and solely neutral particles were measured for six pairs of incoming/exiting angles and for two fixed values of the incoming energy  $E_i$  (4 and 5 keV). To estimate the ion fractions at the elastic peak, we only use a narrow TOF interval close to the high energy onset as it is shown in Fig. 1 (shadowed region).

Theoretical and experimental ion fractions are shown in Fig. 2 as a function of the exit angle. A reasonable good agreement between both results is observed, except for large exit angles ( $\beta = 35^\circ$ ) where a change in the behavior of the experimental data seems to appear. A similar trend is noticed in

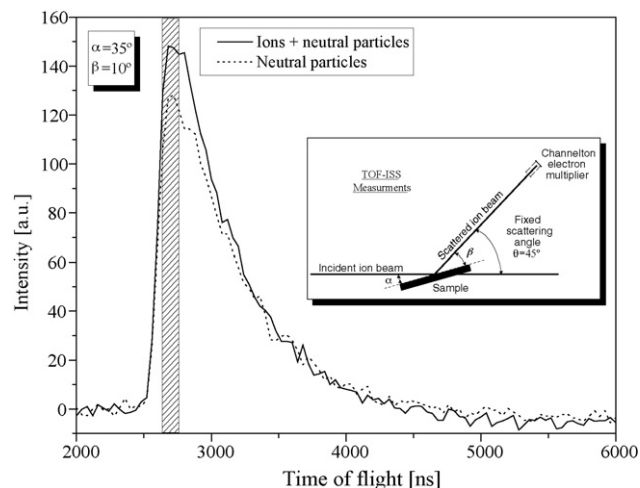


Fig. 1. TOF-ISS spectra of ions plus neutrals (solid line) and exclusively neutral particles (dotted line) for  $\alpha = 35^\circ$  and  $\beta = 10^\circ$  and  $E_i = 4$  keV. The shadowed region indicates the elastic peak width considered. The inset shows a diagram of the TOF-ISS experimental geometry.

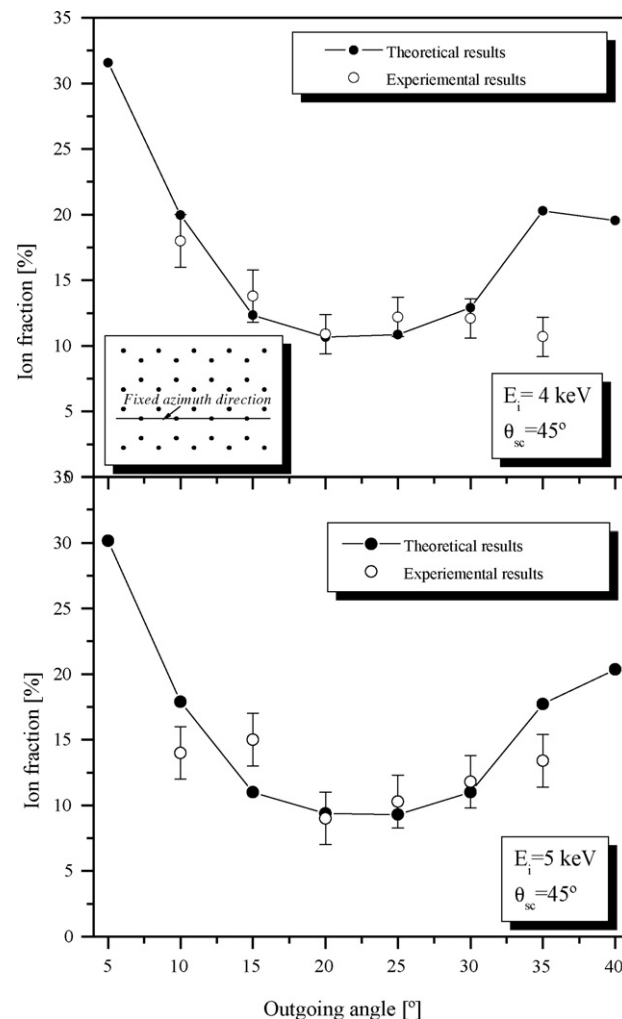


Fig. 2. Outgoing angular dependence of the ion fraction obtained. Theoretical and experimental results are compared for both incoming energies: 4 keV (top) and 5 keV (bottom). Inset top: frontal view of the HOPG surface structure. The projection on the surface of the projectile trajectory assumed in the calculus is indicated.

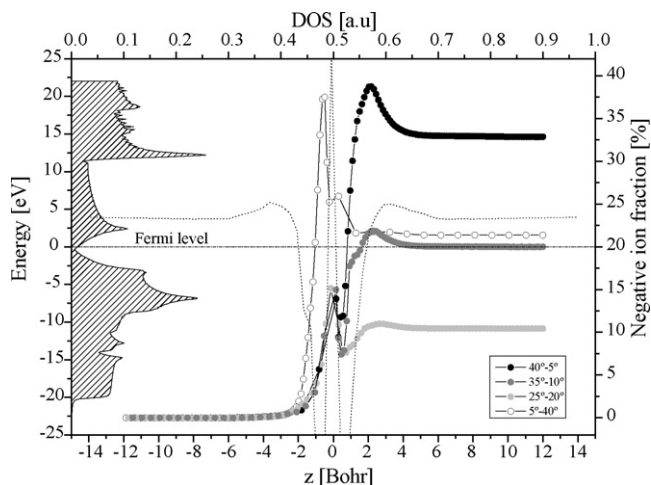


Fig. 3. Affinity energy level (dotted line) of the projectile for  $\alpha/\beta = 25^\circ/20^\circ$  as a function of the normal distance to the surface  $z$ . The black, dark grey, light grey and white points exhibit the normal distance dependence of the calculated negative ion fraction along the trajectory for the incoming/outgoing angles indicated in the figure. The shadowed area corresponds to the HOPG total DOS.

the theoretical ion fractions but arising at a higher exit angle ( $40^\circ$ ).

The calculated evolution of the negative ion fraction as a function of the projectile–surface distance ( $z$ ) is shown in Fig. 3 for four values of the exit angle and a fixed value of the incoming energy (4 keV). The theoretical ion fractions are calculated for a fixed azimuth angle value (see inset of Fig. 2). Negative (positive) values of  $z$  correspond to the incoming (outgoing) trajectory.

For all curves and during the whole trajectory, two different processes can be distinguished: electron capture and electron loss processes. Both processes are more significant at lower angles. Longer projectile–surface interaction times, occurring at grazing trajectories, favor charge transfer, thus explaining the observed behavior.

At the incoming part of the trajectory, the electron capture starts when the projectile affinity level reaches the surface Fermi level. The particular HOPG DOS leads to relatively low ion fraction values (lower than 40%) at the end of this process, compared with the metallic surface case [4]. Afterwards, a sudden fall of the ion fraction is observed in all cases, being, perhaps, a consequence of the abrupt rise of the affinity energy level close to the turning point. At the first part of the outgoing trajectory (for  $z$  values where the affinity energy level is lower

than the Fermi level), the capture process continues. When the affinity level reaches the conduction band, the electron loss process starts. An occupied band DOS higher than the DOS empty band leads to a capture process more sensitive to the outgoing angle than electron loss.

It is also important to notice that main changes in the negative ion fraction evolution are observed at projectile–surface distances lower than 4 bohr. This feature is primarily due to the pronounced localization of the C atoms valence states.

## 5. Conclusions

It is found a satisfactory quantitative and qualitative agreement between calculated and experimental results taking into account the experimental errors, the simplifications of the theoretical model, and the complex nature of the analyzed system. In a more precise calculation the ion fractions could be averaged over all azimuthal directions of the surface (consistent with the polycrystalline nature of the real sample). In this way, a smoother theoretical ion fraction dependence on the outgoing angle is expected, improving the qualitative accordance between theoretical and experimental results.

The calculated ion fraction evolution was qualitatively described taking into account the projectile affinity level and the HOPG total DOS. The semi metallic character of the HOPG DOS seems to play a crucial role into the behavior and magnitude of the negative ion fraction.

## Acknowledgements

We gratefully acknowledge to Dr. C. González Pascual and Dr. Y. Dappe from Universidad Autónoma de Madrid, for providing us the HOPG DOS.

## References

- [1] M. Torralba, P. Bolcato, E. Goldberg, Phys. Rev. B 68 (2003) 075406.
- [2] H. Verbeek, W. Eckstein, R. Bhattacharya, Surf. Sci. 95 (1980) 380.
- [3] K. Tsumori, W. Koppers, R. Heeren, M. Kadodwala, J. Beijersbergen, A. Kleyn, J. Appl. Phys. 81 (1997) 6390.
- [4] M. Gleeson, A. Kleyn, Nucl. Instrum. Methods Phys. Res. B 157 (1999) 48.
- [5] J. Loss, J. Geerlings, Phys. Rep. 190 (1990) 133.
- [6] E. Garcia, C. Pascual, P. Bolcato, M. Passeggi, E. Goldberg, Surf. Sci. 600 (2006) 2195.
- [7] O. Grizzi, M. Shi, H. Bu, J. Rabalais, Rev. Sci. Instrum. 61 (1990) 740.