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Multiple Auger processes in Graphene

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ABSTRACT

Resonant Auger decay processes have been studied by resonant photoemission spectroscopy (resPES) and X-ray absorption spectroscopy (XAS) in Graphene systems. The π*-resonance is used to identify the degree of localization of the lowest π*-orbitals in the conduction band. Localization and lifetime of the photo-excited intermediate state cause the formation of multiple Auger processes. For the Graphene systems we identify two novel Auger decay combinations with a four hole final state: the (S + S) and the (S + S)* decay. We demonstrate that these processes are sensitive for interlayer coupling and interactions with the metallic free electrons of the substrate.

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1. Introduction

Graphene has become the focus of interest of scientists all over the world [1,2]. Properties like ballistic conduction, mechanical strength, elasticity, impermeability, transparency, and thermal conductivity open a wide field for potential new applications. Indeed, a single layer sheet of graphite (Graphene) represents a material that once could replace Si in many areas of communication technologies.

For integrated circuits, especially for transistors, p-doping, n-doping, and contacts to Graphene become necessary. A key function is how to create an electronic contact to the Graphene sheet without destroying its free carrier properties. Direct contact of Graphene with metals or highly doped semiconductors could either introduce screening effects or even open a band gap. The hybridization of Graphene π-states with metal d- and s-states could cause a pinning of free charge carriers in Graphene to the metal substrate.

Angle-resolved photoemission spectroscopy (ARPES) is the method of choice to measure the band structure and linear dispersion of the Dirac cone at the K-point of Graphene [3]. Also X-ray absorption spectroscopy (XAS) is a well-established technique for measuring the electronic structure of the unoccupied states.

Resonant photoemission spectroscopy (resPES) is another technique with a high sensitivity for the element specific density of states. In a complete presentation of a resonant photoemission study (2D resPES diagram) information about both valence band (VB) and conduction band (CB) states is provided. In addition, spectroscopic evidence of resonant decay processes can be used to identify the degree of localization of the states around the Fermi energy.

In 2D resPES diagrams the resonant excitation and decay mechanisms are described by the Kramers–Heisenberg scenario [4]. An electron from the ground state $|g\rangle$ is excited into an intermediate state $\langle j|$ modulated in intensity by the transition operator T_1. The lifetime of the intermediate state Γ_j determines the full width at half maximum (FWHM) of these resonances. The intermediate state will then decay under emission of electrons into a final state $\langle f|$. The transition operator T_2 describes the individual possible decay channels.

XAS spectra of Graphene are reported by several groups with a still ongoing debate of the origin of the Graphene specific spectral features [5–9]. All groups agree that the C1s XAS appears at 285 eV which is the π*-resonance. In addition there is a pre-edge peak below 285 eV, which is commonly observed but diversely discussed. This pre-edge peak of Graphene is attributed to missing carbon atoms and edge effects [9], to the existence of two zero-slope points along $\overline{MK}$ [5], and to doping [7,8].

In this letter we report the X-ray absorption fine structure (XAS) and resPES spectra of both, Graphene flakes and monolayer (ML) Graphene. We will show that at the C1s resonance a combination of individual Auger processes can be observed. We find that the effect of interlayer coupling and of substrate interaction cause a change in the lifetime of the intermediate state which in turn changes the combination of Auger processes. We propose this method to be an extremely sensitive tool for the analysis of the free carrier properties in Graphene.

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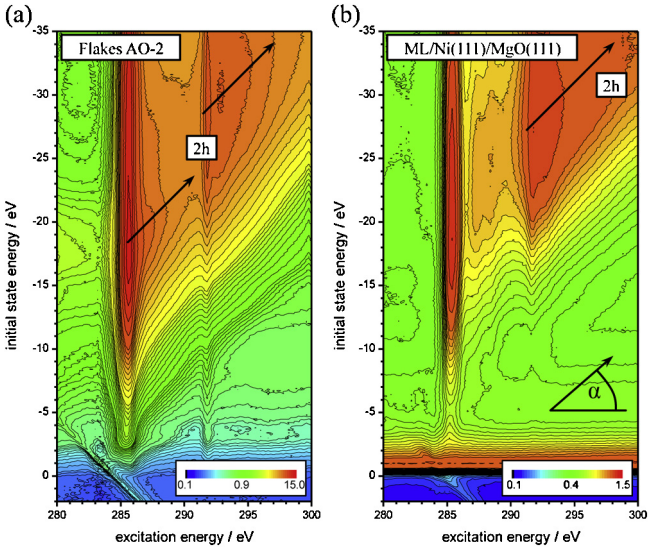

Fig. 1. ResPES diagram of Graphene flakes AO-2 (a) and monolayer Graphene on Ni(1 1 1) (b). The excitation energy is plotted along the *x*-axis and the initial state energy is plotted in *y*-direction. The intensity of the signal is given in logarithmic scale and color scale contours. Black arrows indicate the 2 h Auger decay. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

We also focus on the pre-edge peak, which we identify as low energy Auger decay involving states at the Fermi energy of the metal substrate.

2. Materials and methods

Spectroscopic measurements on the Graphene samples were carried out at the U49/2 beamline at BESSY II, Berlin. A SPECS Phoibos 150 was used as the electron analyzer and a 1D delay-line detector as the electron detector. All samples were characterized by means of photoelectron (PES) and X-ray absorption spectroscopy [10]. The resolution of the spectrometer used was 70 meV. Together with the photon resolution (30 meV at the carbon K-edge) we have a resolution for PES (VB) of around 80 meV and for XAS (CB) measurements of 30 meV. All spectra are corrected for the incoming photon flux.

For measuring the resPES VB spectra at the C1s edge (resPES diagram) the photon energy was varied over a wide range (280–300 eV) by sweeping the undulator gap and the monochromator in parallel.

Graphene flakes type AO-2 and AO-4 were obtained from Graphene-supermarket (NY). The flakes were annealed at 1000 °C under nitrogen for 30 min. In this way high quality Graphene flakes were obtained [11]. Our AFM studies reveal the average diameter of these films to be in the order of 20 μm.

As a reference sample a high quality monolayer Graphene on Ni(1 1 1) was prepared by a chemical vapor deposition (CVD) process. The Ni(1 1 1) substrate layer was grown epitaxial on a MgO(1 1 1) substrate [12]. The sample was cleaned in UHV by heating to elevated temperatures to remove hydrogen and carbon contaminations.

3. Results

The two Graphene samples, Graphene flakes and monolayer Graphene on Ni(1 1 1) (ML/Ni(1 1 1)), were studied by resPES. A set of 101 VB spectra (initial state energies between −35 eV and 2 eV) at the carbon K-edge was recorded. These spectra are plotted in a 2D intensity contour plot and are displayed in Fig. 1.

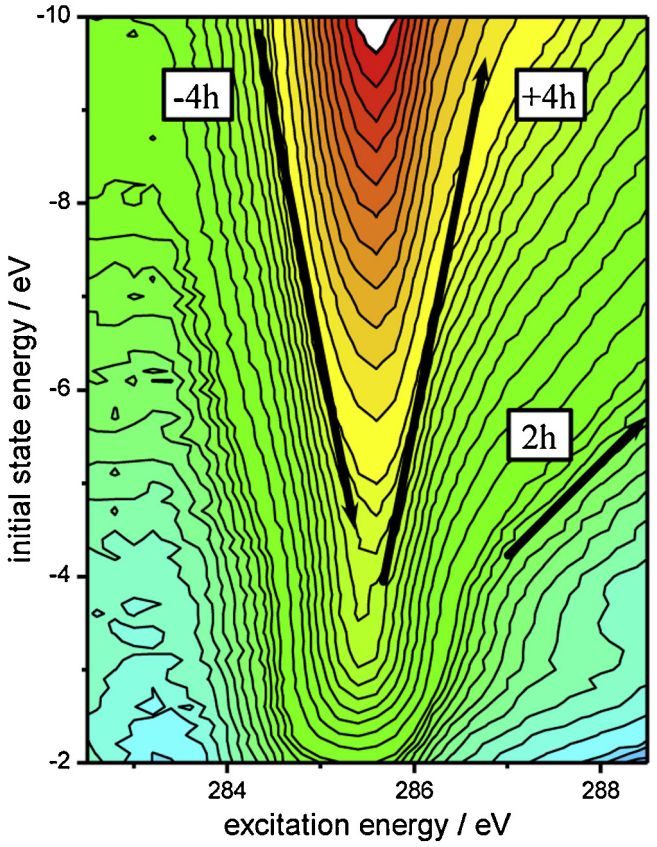

Fig. 2. Close-up resPES diagram of graphene flakes AO-2. The motion of the ±4 h Auger decay in the vicinity of the first π* resonance of 285.5 eV is indicated by two black arrows as derived from the propagation of the contour lines. Approximately 1.5 eV above the resonance at a excitation energy of 286 eV the motion of the 2 h Auger decay can be observed as indicated by a black arrow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

In the data the first (π*-) resonance appears at around 285.5 eV and 285.2 eV for the Graphene flakes and ML/Ni(1 1 1), respectively. There is a second (σ*-) resonance at an excitation energy of 292 eV. The plots are dominated by the appearance of the broad C-KLL Auger emission, the main emission appears at a constant kinetic energy of 263 eV (Graphene flakes) and 264 eV (ML on Ni(1 1 1)) which is indicated by the black arrows.

In the spectra of Graphene flakes (Fig. 1a) the 2 h KLL spectator decay starts at the resonance energy of 285.5 eV. We find its appearance above the π*- with a kinetic energy of $E_{\mathrm{kin},\pi^*} = 267$ eV and above the σ*-resonance with $E_{\mathrm{kin},\pi^*} = 263$ eV.

At the first resonance at 285.5 eV we observe a V-shape Auger decay. A close-up of the particular region of interest is shown in Fig. 2. As indicated by the black arrows (±4 h) at the lower binding energy end close to the Fermi energy the Auger decay propagate under an angle $\alpha = \pm 78.75^\circ$. The Auger angle α is defined by the slope of the $E_{\mathrm{bind}}(\hbar\omega)$ diagram as indicated in Fig. 1b. It can also be clearly derived from the motion of the constant count contour lines of Fig. 2. In a previous work it was found that the angle α represents the integer hole final state of the Auger decay [13]. Graphene flakes of a lower quality (AO-4, data not shown) show a reduced intensity of the ±4 h Auger decay. This is evident by an increased intensity in the exciton resonance [11].

It is remarkable that the general Auger pattern for the ML on Ni(1 1 1) samples exhibits significant differences (Fig. 1b). In particular, the 2 h KLL-Auger decay is observed only above the σ*-resonance with $E_{\mathrm{kin},\sigma^*} = 264$ eV. At the π*-resonance above 285.2 eV

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