Nuclear Inst, and Methods in Physics Research B 422 (2018) 63–67

Contents lists available at ScienceDirect

Nuclear Inst. and Methods in Physics Research B

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

The role of radiative de-excitation in the neutralization process of highly charged ions interacting with a single layer of graphene

J. Schwestka[a,*], R.A. Wilhelm[a,b,*], E. Gruber[a], R. Heller[b], R. Kozubek[c], M. Schleberger[c], S. Facsko[b], F. Aumayr[a]

[a] TU Wien, Institute of Applied Physics, 1040 Vienna, Austria
[b] Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, 01328 Dresden, Germany
[c] University Duisburg-Essen, Faculty of Physics and CENIDE, 47057 Duisburg, Germany

ARTICLE INFO

Keywords:
Slow highly charged ions
Graphene
X-ray emission

ABSTRACT

X-ray emission of slow (< 1 a.u.) highly charged Argon and Xenon ions is measured for transmission through a freestanding single layer of graphene. To discriminate against X-ray emission originating from the graphene's support grid a coincidence technique is used. X-ray emission of 75 keV Ar^{17+} and Ar^{18+} ions with either one or two K-shell vacancies is recorded. Using a windowless Bruker XFlash detector allows us to measure additionally Ar KLL and KLM Auger electrons and determine the branching ratio of radiative vs. non-radiative decay of Ar K-shell holes. Furthermore, X-ray spectra for 100 keV Xe^{22+}-Xe^{35+} ions are compared, showing a broad M-line peak for all cases, where M-shell vacancies are present. All these peaks are accompanied by emission lines at still higher energies indicating the presence of a hollow atom during X-ray decay. We report a linear shift of the main M-line peak to higher energies for increasing incident charge state, i.e. increasing number of M-shell holes.

1. Introduction

The interaction of slow ($v \ll v_0$ … Bohr velocity) highly charged ions (HCI) with solid surfaces leads to charge exchange between the target and the projectile followed by the de-excitation of the ion during and after the interaction process. Already at a distance of several Ångströms from the surface the ion starts to capture electrons into highly excited Rydberg states well explained by the classical over-the-barrier model [1]. Thus, an almost neutralized projectile with empty inner shells, a so-called “hollow atom”, is formed. Studies of the charge state of slow highly charged ions after the transmission through 5 nm thin carbon films [2] showed exit charge states of the projectiles far away from their equilibrium charge state. By evaluating the mean of the exit charge state distribution as a function of the projectile velocity the authors of [2] could derive a charge equilibration time of less than 7 fs. A generally accepted model describing the de-excitation processes of hollow atoms exists since more than 20 years [3], although some open questions regarding a too slow de-excitation cascade remain (e.g. [4,5]).

Recently performed experiments using target materials of only 1 nm thickness [6–8] or the ultimate thin target graphene [9] brought this “bottleneck problem” up again in the understanding of the observed fast de-excitation of a hollow atom. By studying the electronic response of a freestanding single layer of graphene (SLG) to the large external field of an approaching HCI an almost complete neutralization of the ion within a few femtoseconds could be concluded [9]. In this short time frame dozens of electrons are not only transferred from the target to the projectile, but also stabilized in the ground state of the ion, i.e. not lost by auto-ionization. The step by step de-excitation cascades presented in [3] to explain the de-excitation process of the hollow atom would be far too slow. Auger/autoionization rates in the order of $10^{16} - 10^{17}\,s^{-1}$ would be required to reach the observed neutralization within femtoseconds. Therefore, the model had to be refined and the interatomic coulombic decay (ICD) [10] process was proposed [11] as the responsible process for the observed fast de-excitation of a HCI. In the suggested model, electrons from high Rydberg states are quenched into low core states of the projectile while the released energy is transferred to electrons of the surrounding target. The ICD process gives rise to the emission of valence electrons into the continuum originating from next neighbouring or even next-nearest neighbouring atoms of the target [11]. However, so far it is not clear whether the ICD process directly populates the ground state or just low lying excited states, which still have to decay by X-ray or Auger emission.

For inner-shell transitions Auger rates increase to $10^{14} - 10^{15}\,s^{-1}$ as well as radiative transition rates for K and L-shell filling of up to $10^{14}\,s^{-1}$ are possible [12]. As soon as holes in the L, M and N shells are

* Corresponding authors at: TU Wien, Institute of Applied Physics, 1040 Vienna, Austria (R.A. Wilhelm).
E-mail addresses: schwestka@iap.tuwien.ac.at (J. Schwestka), wilhelm@iap.tuwien.ac.at (R.A. Wilhelm).

https://doi.org/10.1016/j.nimb.2018.02.022
Received 14 October 2017; Received in revised form 19 January 2018; Accepted 20 February 2018

filled, radiative and non-radiative processes become likely to contribute in the very last steps of the neutralization process. In the present work, we therefore measure X-ray and Auger electron emission for hydrogen-like and bare Ar ions from SLG and estimate the branching ratio of these two competing channels. A slight predominance of emitted Auger electrons is found for both cases. The measured X-ray spectra are compared with atomic structure code calculations [13,14] as well as with experimental data recorded for Argon ions interacting with metal surfaces [15]. To further study the radiative de-excitation channel X-ray emission spectra resulting from the impact of highly charged Xenon ions on the graphene sample are presented.

2. Experimental setup

The measurements were performed at the Ion Beam Center of the Helmholtz-Zentrum Dresden-Rossendorf, where highly charged ions are produced in a room-temperature electron beam ion trap (EBIT) [16]. An analyzing magnet is used for charge state separation of the extracted ion beam, which is focused into the target chamber by electrostatic lenses. Inside the experimental chamber an electrostatic analyzer with an energy resolution of $\Delta E/E = 1.5 \times 10^{-3}$ and an acceptance angle of 1.6° is mounted for charge state and energy loss measurements of the projectiles after the transmission through thin target samples. After passing the electrostatic analyzer, the ions as well as neutral particles are counted in two different channeltrons. Close to the interaction region of the ion beam with the target a windowless Bruker XFlash silicon drift detector (SDD) is mounted for measuring emitted X-rays as well as Auger electrons with energies above 700 eV. The detector has an energy resolution of $\Delta E = 140$ eV at 5.9 keV and is calibrated by using Mn-K_α and Mn-K_β emission lines of a mounted ^{55}Fe source. Fig. 1 shows a sketch of the described experimental setup.

To discriminate X-rays and electrons emitted from ions interacting with the target support a coincidence technique is used. This ensures that only a signal at the X-ray detector is recorded if there is a corresponding ion signal registered at the channeltron after transmission through the monolayer film.

Freestanding SLG samples of high quality were fabricated at the University of Duisburg-Essen. Commercially available graphene (Graphenea) grown via chemical vapour deposition (CVD) on a copper foil was placed on a transmission electron microscopy (TEM) grid with an additional Quantifoil support on top. The copper foil was removed by etching and remaining contaminations were eliminated by heating the samples at 260 °C in active carbon (for more details see [17]). No polymer coating was used during the transfer process.

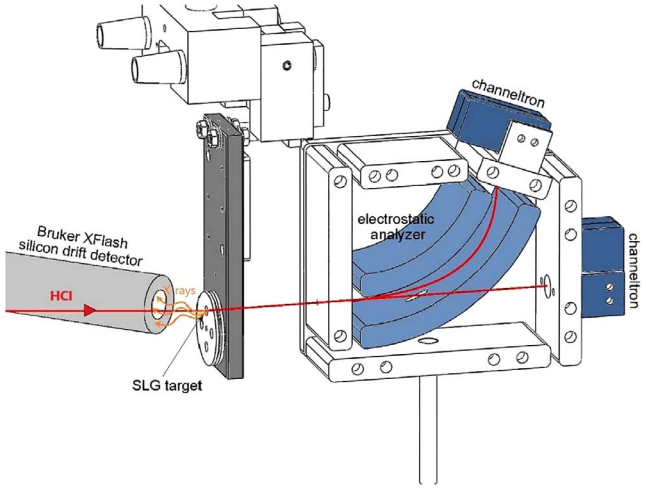

Fig. 1. Sketch of the experimental setup. The collimated ion beam is passing the sample, mounted on the rotatable target holder, before it enters the electrostatic analyzer and hits one of the channeltrons.

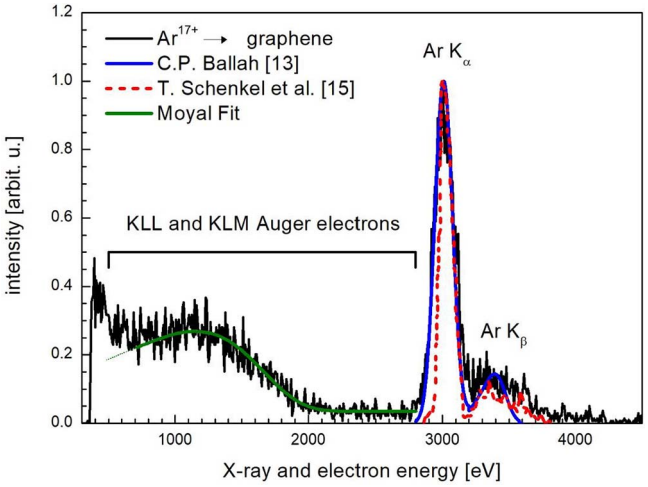

Fig. 2. X-ray, KLL and KLM Auger electron emission spectrum following slow H-like Ar^{17+} ions traversing a SLG. The measured X-ray spectrum (black solid curve) is compared with atomic structure code calculations [13] (blue curve) and with recorded X-ray emission resulting from slow Ar^{17+} ion impact on a Be target [15] (red broken curve). A Moyal distribution (green curve) to fit the energy loss in the dead layer of the detector is used to estimate the contribution of KLL and KLM Auger electrons to the spectrum. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results

The SLG sample was irradiated with 75 keV Ar^{17+} and Ar^{18+} projectiles as well as 100 keV $Xe^{22+} - Xe^{35+}$ ions. X-ray emission spectra were recorded in coincidence with projectiles transmitted through the monolayer graphene target.

The emission spectrum of slow hydrogen-like Ar^{17+} ions interacting with a graphene sheet is presented in Fig. 2. The filling of one K-shell vacancy results in peaks in the X-ray spectrum between 2800 eV and 4000 eV. Assuming a Gaussian shaped detector function with a full width at half maximum (FWHM) of 140 eV (energy resolution of the Bruker XFlash detector at an energy of 5.9 keV for Mn-K_α) the observed spectrum can be very well reproduced by atomic structure code calculations performed by Bhalla [13]. For various electronic configurations of the Ar ion (i.e. population of excited states in the L, M and higher shells) shifts in the K_α and K_β emission energies have been calculated as well as the relative intensities of these lines. Comparison with our experimental data indicates that the filling of the K-shell occurs while some vacancies in the L- and M-shell of the Ar ion are still present. X-ray emission for the interaction of Ar^{17+} with a Be sample has previously been measured by Schenkel et al. [15] using a calorimeter detector. The comparison of these results with the presented data shows almost no differences in whether a 3D solid or only a monolayer thick target is used. Only a small broadening of the K_α peak towards lower energies in case of the SLG target can be observed, which might result from a poorer relative detector resolution $\Delta E/E$ at lower energies than the Mn-K_α emission line. Our data indicate that the radiative de-excitation of the initially highly charged Ar ion occurs before the filling of the L-shell is complete. According to [13] the main peak of the spectrum at 3006 eV would correspond to about 3 L-shell holes present during the $2p \rightarrow 1s$ transition.

Since a windowless silicon drift detector is used for the X-ray measurements also electrons with energies above 700 eV can be registered, which otherwise would be unable to pass a Be window at the entrance of the detector. Emitted Ar KLL and KLM Auger electrons due to the de-excitation process of the HCI can be seen in Fig. 2 as a broad distribution above the noise level and below 2800 eV. The KLL and KLM Auger electron emission results in a multiple peak structure with energies between 2506 eV and 2926 eV [18], which can no longer be