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Sub-eV ion deposition utilizing soft-landing ion mobility for controlled ion, ion cluster, and charged nanoparticle deposition

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ABSTRACT

Sub-eV ion deposition via soft-landing ion mobility has been utilized for a variety of applications. It has allowed for the deposition of a dielectric material onto graphene without introducing defects into the lattice structure. This deposition technique has also been used for surface enhanced Raman studies. Deposited silver has also been used as an alternative MALDI matrix for low mass compounds and shows promise for imaging applications.

1. Introduction

Controlled ion deposition via soft-landing ion mobility has allowed for the deposition of ions, ion clusters, and nanoparticles for a variety of applications. Soft-landing refers to deposition that occurs with limited energy so as to not induce fragmentation of the species [1]. The energy regimes considered for soft-landing are the hyperthermal (1–100 eV) and thermal regimes (below 1 eV) [2,3]. Soft-landing has been utilized for the study of various entities such as biological molecules, organic material, organometallics, and metal clusters [1,4]. The ability to alter deposition parameters and manipulate ion trajectories allows for these controlled experiments. Using soft-landing for the deposition of a variety of materials has opened research avenues regarding other techniques such as surface-enhanced Raman spectroscopy (SERS) and surface modification to create new or alter properties of current materials [5–9].

The current soft-landing ion mobility (SLIM) system has been characterized to better understand the nature of species being landed and their dependence on experimental parameters. The duration of deposition was expected to mainly affect surface coverage, with longer deposition times it is expected that more material would be deposited onto the surface. Changes in the pressure of the buffer gas can alter the size and surface coverage significantly. Diffusion is a direct result of interactions of the ions with the neutral buffer gas, and changes in the pressure of the buffer gas alters the likelihood of collisions between ions and the gas molecules. Therefore, higher pressures increase the potential for losses while traveling towards the landing surface. Diffusion increases with increasing pressure, which in turn decreases the amount of material that is deposited. An increase in pressure can cause an increase in the size of particles deposited [10]. The type of gas can alter the material and create oxides or nitrides, or affect the speed of ions through the drift region [11–13]. Altering the laser energy employed for the ablation event also is expected to have a significant effect on the amount of material deposited, as more material will be ablated initially. Characterizing the influence of SLIM parameters on the soft-landed species will allow for directed experimental design to achieve specific size, morphology, or spatial distribution.

Soft-landing hafnium oxide onto graphene has enabled the production of a p-type material. The low energy deposition of hafnium oxide did not induce any defects into the graphene lattice. Graphene has unique properties, both electronic and structural, that make it a material of interest for electronic devices [14–19]. Graphene is a semimetal with a zero [20,21] or very low bandgap [22,23], meaning there are no or limited energy ranges where electron states do not exist. One of the prerequisites to developing a practical device is the presence of a bandgap thereby allowing the device to be operated in a switched manner. Altering the bandgap of graphene has been done by: affecting confinement of charge

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carriers [24], molecular doping, manipulating strain, and doping by metallic or insulating adsorbates. The deposited ions on graphene act as electron acceptors, taking electron density from the graphene creating electron holes, altering the bandgap, and ultimately creating a p-type material.

The use of soft-landed silver nanoparticles as an alternative matrix for matrix-assisted laser desorption ionization (MALDI) has shown promise, however, a better understanding of deposition conditions may help improve these experiments. This technique has also been employed for creating self-assembled monolayer (SAM) surfaces that can be reused for SERS analysis [25]. Silver is prone to oxidation and generally requires stabilizers to be used for nanoparticle formation, however soft-landing allows for deposition of silver directly onto the sample [26–33]. This avoids the need for stabilizers and the more common and time consuming solution based synthesis [34–37]. Fig. 1 depicts the mobility cell showing the separation of species within the drift region with the ability to land or detect selected species.

2. Metal-oxide deposition for doping graphene

2.1. Materials and methods

Hafnium oxide deposition on graphene was investigated using SLIM. The SLIM system, developed by our group has been described in full detail elsewhere [1,38]. Briefly, a linear DC field is applied across a drift tube consisting of resistively coupled stainless rings. Ions were generated by the ablation of a metal target with a 532 nm Nd:YAG laser (Minilite II, Continuum, Santa Clara, CA), operated at 2 Hz rep rate in the presence of a buffer gas. A buffer gas, in this case, 5% O_2 in He, is leaked in at a particular pressure to generate the desired ion kinetic energy. Ions, under the influence of the applied field and buffer gas are separated according to their collision cross section. Ions are directed towards a landing surface for collection at the end of the drift tube. Ionization is achieved via pulsed laser vaporization of a solid metal target, in this case a hafnium rod. Graphene samples were produced with mechanical exfoliation of ZYB-grade highly ordered pyrolytic graphite (HOPG, SPI) onto a silicon substrate coated with a 300 nm oxide layer following the method of Geim and co-workers [39]. Exfoliation was completed under ambient conditions (71 °F, 58% relative humidity). Upon completion of exfoliation the graphene samples were examined by optical microscopy to determine the spatial orientation of the graphene. Pristine samples were then studied using micro-Raman spectroscopy with 532 nm incident radiation and the presence of monolayer graphene (MLG) was confirmed by the ratio of I_G/I_{Si} [40,41] as seen in Fig. S1 of the Supplementary data. Raman spectra were collected using a Thermo-Electron Nicolet Almega XR (Waltham, MA).

After Raman confirmation, the samples were placed in the SLIM chamber, and the chamber was evacuated to below 20 mTorr. Once reaching this pressure, the buffer gas is introduced to obtain a pressure of 2 Torr. After pressure stabilization, a field of 22.31 V/cm is applied across the drift cell and a 190 V bias is applied to the backing plate behind the ionization source. This voltage is to deflect and propagate the charged species through the mobility cell. Pulsed laser vaporization was carried out at 50% laser energy with a 2 Hz rep rate. In all experiments the laser was rastered along the surface of the metal target to ensure a consistent ablation event. This method is consistent with previous experimental reports for the in situ production of hafnium oxide [42–44]. Soft-landing was completed in a step-wise fashion over the course of 7 h, with post-landing Raman analyses being conducted at deposition intervals of 15 min for the first hour, and 1 h increments thereafter. Post deposition analysis also included scanning electron microscopy (SEM), Auger spectroscopy, and X-ray photoelectron spectroscopy (XPS). SEM micrographs were obtained using an FEI Quanta ESEM to confirm particles on the surface. Further analyses of these particles were done using a PHI 670xi Auger Nanoprobe (Chanhassen, MN) at 5 keV electron energy and a PHI 5000 Versaprobe (Chanhassen, MN) equipped with the Aluminum K-α line with 20.0 μm spot size for XPS analysis

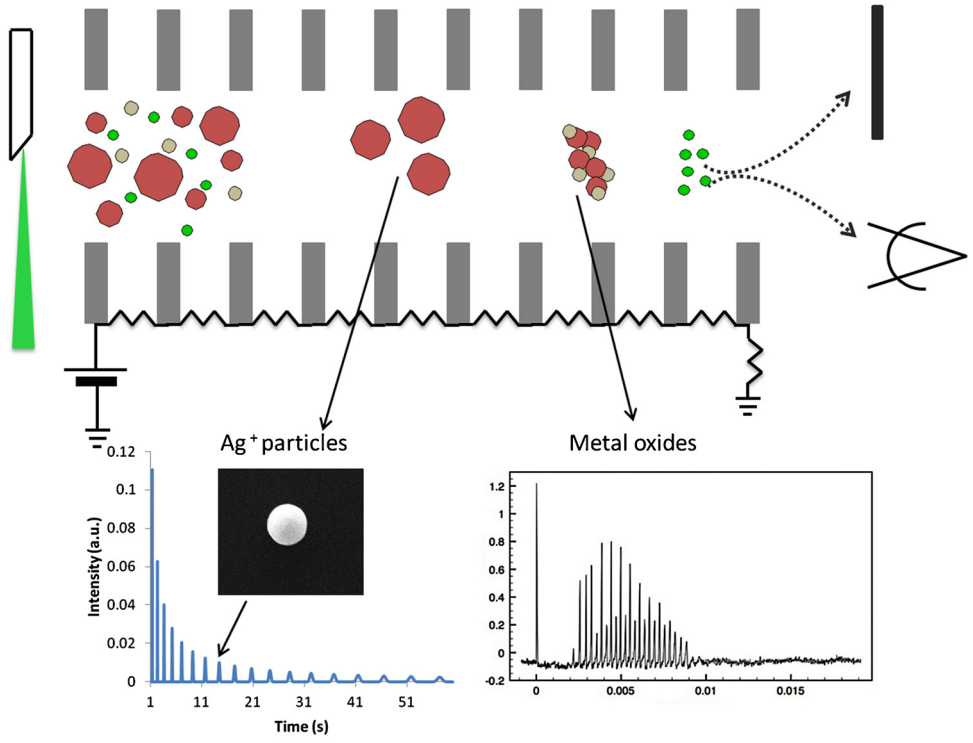

Fig. 1. Schematic of the separation of different ions within the mobility cell, showing that ions can be directed to either a landing surface or detector.