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CLUSTER ION IMPLANTATION AND RADIATION DAMAGE IN GRAPHITE AND DIAMOND

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Ion-beam treatment of materials is one of the very widely applied techniques for numerous research and industrial purposes. Along with traditional monomers, atomic or molecular clusters (aggregates of atoms or molecules) have attracted considerable attention during the last two decades [1-4]. For developing successful applications of clusters beams, a theory of cluster stopping in matter is required. Unfortunately, the existing theory for conventional ion implantation can be applied to cluster ions only for a very limited number of cases due to the fact that cluster is an aggregate of weakly bonded atoms or molecules providing multiple collision effect with target. Therefore, main emphasis of this paper is put on the development of scaling laws for cluster implantation.

The main material under the discussion is graphite or highly ordered pyrolytic graphite (HOPG). Graphite is chosen for modelling and experiments because it has an atomically smooth surface that makes it easy to resolve very small features on the sub-nm scale. The surface is also relatively chemically inert, i.e. properties and structure of the deposited clusters are not much disturbed. Layered structure of graphite with strong covalent bonds in the graphene layers and very weak van der Waals interactions between them is an interesting type of crystalline arrangement for modelling of clusters implantation. The data on implantation into graphite are compared with the results of cluster implantation into diamond, another allotropic form of carbon with strong and directional covalent bonds. This material is of significant practical interest. Some of its electronic characteristics, for instance, the high mobility of electrons and holes, low noise and leakage current as well as extremely high thermal conductivity make this material attractive for high-power and high-frequency electronics [5]. Diamond also is a potential platform of solid-state quantum devices.

Elastic collision of an accelerated monoatomic ion with lattice atoms causes a knock-on effect: the displaced atoms can be sputtered from the surface or become recoils contributing into the formation of a displacement cascade in the target [6]. Very often crater formation is observed on impact of energetic clusters [7, 8]. The efficiency of crater formation is dependent on cluster size and kinetic energy. Substrate material also plays an important role.

Higher density, melting (or sublimation) point and larger atomic displacement energies provide less favourable conditions for crater formation. Diamond is a good example of a material on which it is difficult to produce craters [9]. Graphite is another allotropic form of carbon, having a layered structure with strong covalent bonds (significant displacement energies of ca. 12-20 eV along *c*-axis are required) in graphene planes and weak van der Waals interactions between the layers. Therefore, the graphite structure responds very elastically to cluster impact: the collision induces oscillations of the graphene planes [10]. For the case of relatively small in size Ar_n (n = 16 and 41) colliding HOPG with energies up to 16 keV/cluster, the oscillations have very little influence on the structure outside the immediate impact region with primary displacement cascades, although their amplitude could be as large as the distance between two neighbouring planes. Thus, a crater can be formed only at the initial stage of impact. The elastic behaviour of graphene sheets at a later stage causes efficient closure of the craters and only disordered areas are finally formed. These areas are found by STM as tiny bumps (Fig. 1a). Dimensions of these features are in good agreement with the lateral sizes of damaged areas predicted by molecular dynamics (MD) modelling. It is worth noting that craters can be formed on HOPG but the clusters should be larger and they should have high kinetic energies, in order to be able to provide high energy density transfer to the graphite target [11].

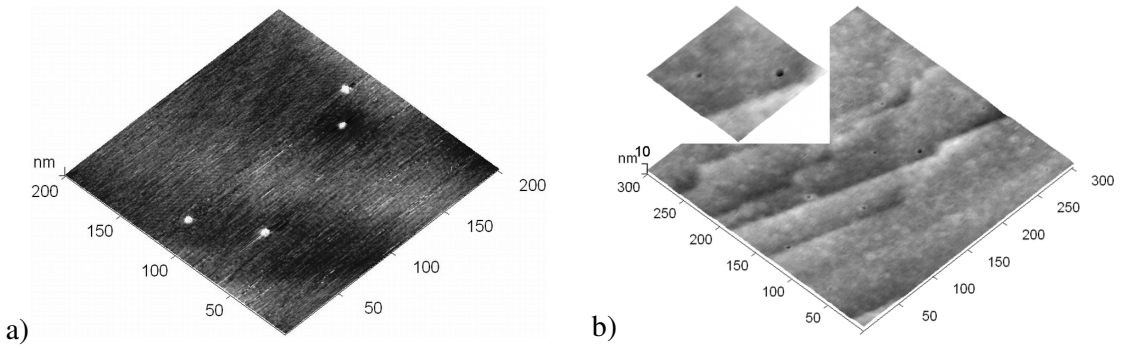

Figure 1. (a) STM image of HOPG implanted by Ar_{41}^+ cluster ions with energy of 4.1 keV and (b) AFM image of diamond implanted by Ar_{27}^+ cluster ions with energy of 12 keV.

The threshold energy needed to displace a carbon atom in diamond is much higher (between 35-80 eV) [12] than in graphite. The simulations showed no indication for molten diamond under the impact at energies up to 21 keV for Ar_{27} [9]. Thus, there is a low probability for crater formation through the mechanism involving compression, local melting and following liquid flow as often the case in other materials [8]. The cluster bombardment of diamond can cause craters only through direct sputtering of the surface atoms. Experimentally, a few cases of craters with diameters of 5-7 nm were found using atomic

force microscopy (AFM) after the bombardment by Ar_{27}^+ with energies up to 15 keV as shown in Fig. 1b. In some cases small hillocks with height of 0.5-2.0 nm and basal diameter of 10-15 nm were observed which could be unresolved (due to tip convolution effect) craters.

We have shown previously that the projected ranges R_p of cluster constituents implanted with keV energies follow the square root of energy $E^{1/2}$ dependence [13, 14]. Since cluster momentum $p \sim E^{1/2}$, it was suggested to scale R_p with momentum that ledto the linear scaling law. The use of momentum allows considering the cluster size (through its mass) together with the energy, thus, using only one physical quantity. However, as one can see in Fig. 2, the linear fits for different sizes of argon clusters have different slopes. Similar dependences were earlier observed for cobalt clusters [15]. This discrepancy can be removed by considering one more important parameter: an area of cluster-matter interaction. It can be found as a cross-sectional area of the cluster projected on the surface. Dividing the cluster momentum by this area, allows to introduce the scaled momentum [13]. It was found that the experimental values of depth of radiation damage (which is approximately equal to R_p for keV energy clusters) for different cluster sizes and different cluster species fall on the same fit straight line vs scaled cluster momentum as shown in Fig. 3 for the implantation into HOPG [16]. This provides very strong support for the assertion that the cluster implantation depth is a linear function of momentum per unit surface area.

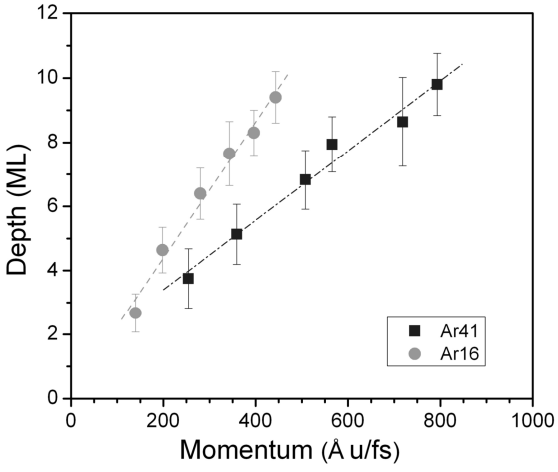

Figure 2. Dependence of depth of radiation damage in HOPG on momentum of implanted size-selected Ar_n cluster ions.

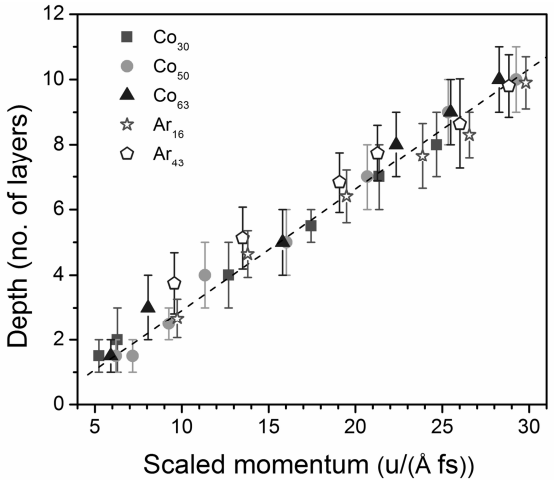

Figure 3. Dependence of depth of radiation damage in HOPG on scaled momentum of implanted size-selected Ar_n and Co_n cluster ions.

It is worth mentioning that correct estimation of the cluster cross-section is an important point. For metal clusters a spherical cluster approximation works pretty well. It does not, however, provide a suitable approach for small rare gas clusters (Ar in our case) since the

charge changes the geometrical configuration of atoms in the cluster. It was suggested by Haberland and co-workers [17] that in argon cluster ions with $n \geq 6$, the charge is distributed among 4 core atoms. This ion core is surrounded by rings or "crowns" of adatoms. Theoretical calculations showed that the bond length shrinks down to ca. 2.45-2.99 Å in the ion core [18, 19]. The atoms surrounding the charged core become polarized thus providing an additional attractive interaction reducing the bond length and distorting the shape of the cluster. For example, the Ar_{16}^+ cluster ion is predicted to be slightly elongated along the charged core (see Fig. 4) [18]. For the Ar_{41}^+ cluster ions, we used the lowest energy geometry for the Ar_{43}^+ cluster ion suggested in [19]. In both cases the cluster shapes could be quite well approximated by ellipsoids. The mean cross-section values were found applying the orientations of the impacting cluster giving the smallest and the largest projected areas on the surface. Only through the consideration of "compressed" clusters with the distorted shape we were able to calculate the scaled momenta which could be fitted by one line shown in Fig. 3.

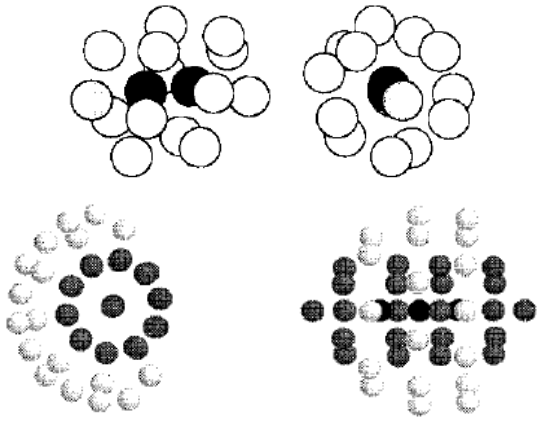

Figure 4. Most stable structures of Ar_{16}^+ (top) and Ar_{43}^+ (bottom) cluster ions obtained from calculations including polarization effect. Dark circles show charged core. According to [17, 18].

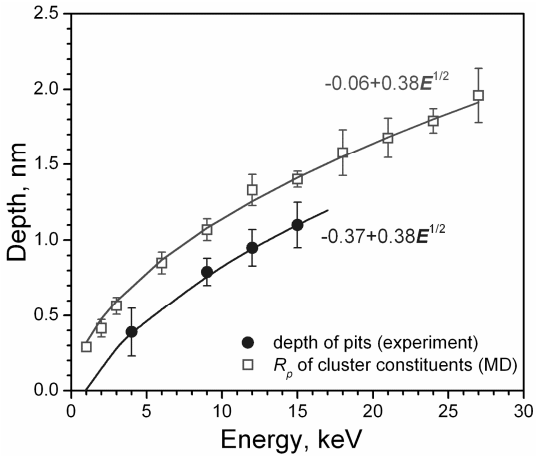

Figure 5. Calculated R_p and experimentally measured depth of damage on impact of Ar_{27} clusters as a function of kinetic energy.

Our recent experimental study of keV-energy argon cluster implantation in diamond showed that depth of radiation damage follow the $E^{1/2}$ dependence [9, 20]. MD simulations also show ($a + bE^{1/2}$) fitting for R_p of cluster constituents, where a and b are the variables. Both curves can be seen in Fig. 5. The difference in depth between the experimental and simulated data is due to the fact that the depth of the etched pits (which were used to measure the depth) corresponds to strongly damaged areas of diamond (probably, fully amorphized ones), which is not the same as the mean depth of penetrated cluster constituents in the simulations. One can also see in the figure that experimental curve crosses the energy axis at

948 eV. Thus, we can suggest a displacement energy of ca. 35 eV/atom for Ar_{27} clusters impacting diamond.

In conclusion, the results obtained on the implantation of argon clusters in diamond show strong similarity to the stopping behaviour of rare-gas, semiconductor, and metal clusters in graphite and demonstrate the same scaling law in which both depth of radiation damage and mean projected range of cluster constituents linearly depend on cluster momentum.

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