



# MD study on high-energy reactive carbon and oxygen cluster impact leading to surface erosion on diamond

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## Abstract

Molecular dynamics (MD) simulations of single  $\text{Ar}_n$ ,  $(\text{CO}_2)_n$ ,  $(\text{C}_3)_n$  and  $(\text{O}_2)_n$  cluster impacts ( $n \simeq 960$ ) on a diamond (111) surface are performed in order to investigate the surface erosion process. Unlike the other three impacts which result in a remarkable emission only at higher cluster acceleration energies at  $E_a \geq 75$  keV, the  $\text{O}_2$  cluster impact induces a significant effect from a lower acceleration energy  $E_a$  of 30 keV on, and the erosion rate increases almost linearly with the increase of the acceleration energy. These differences are ascribed to the reactive emission pattern via the production of CO and  $\text{CO}_2$  molecules. The erosion rate per molecule seems to be expressed as a linear function of the impact velocity minus a threshold velocity independent of the cluster size for the  $\text{O}_2$  cluster impacts.

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## 1. Introduction

Solid surfaces may be effectively modified by using atomic and molecular cluster beams through polishing or physical as well as chemical erosion

[1–4]. The authors have applied highly accelerated ionized cluster beams for micro- and nano-scale surface structuring [5–7], where clusters consisting of about 1000  $\text{CO}_2$  molecules are accelerated to up to 100 keV/cluster and continuously impact on surfaces of diamond, silicon, glass and Teflon films. The reactive enhancement of the surface erosion was clearly shown in the difference in the erosion rates between  $\text{CO}_2$  and argon cluster impacts, with a factor of 3.63 in the case of diamond, while the eroded surface was remarkably smoother for the argon cluster impact [7]. The authors have also performed molecular dynamics (MD) simulations

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of single  $\text{Ar}_n$  or  $(\text{CO}_2)_n$  ( $n \simeq 960$ ) cluster impacts on a diamond (111) surface [8–10]. For a cluster impact energy  $E_a$  of 100 keV/cluster, the formation of a hemispherical crater and two or three-layered induced shockwaves were observed at the early stage of the impact process. Rebounding hot fluidized carbon material was then seen to replenish the transient crater very quickly until 2 ps, with a central peak appearing as a long time phenomenon only in the case of a  $\text{CO}_2$  cluster impact. The reactive enhancement of the surface erosion via the  $\text{CO}_2$  cluster impact was only achieved for  $E_a \geq 75$  keV where a strong CO signal in the spectrum of the emitted fragments was observed, while the surface of the relaxed crater was more densely packed and smoother in the case of the argon cluster impact [9]. Considering the correlation between the erosion effect and the strong CO signal of the emitted fragments, oxygen atoms seem to play an important role in the reactive erosion.

In this study, MD simulations of  $\text{O}_2$  and fictitious  $\text{C}_3$  cluster impacts on a diamond (111) surface are further performed with the acceleration energy  $E_a$  up to 100 keV/cluster in order to investigate the effect of oxygen and carbon atoms in the reactive erosion process, proving the  $\text{O}_2$  cluster to act as a more effective erodant. In addition, the size effect in the erosion by  $\text{O}_2$  cluster impacts is examined.

## 2. Simulation methods

The simulation methods applied are almost the same as in our previous reports [8–10]. Briefly, the empirical potential function proposed by Brenner [11] is adopted for the interaction among carbon atoms with a slight simplification [12], while the interaction potentials of C–O and O–O are derived appropriately from Brenner’s formula [9]. Lennard-Jones potentials are adopted for C–Ar and Ar–Ar interactions. The impact target of diamond (111) surface consists of a hexagonal internal region and an external region with 758,440 and 308,240 carbon atoms, respectively, where only 1/6 of the external region is simulated to reduce the calculation time [9]. The appropriateness of this modeling was confirmed elsewhere [10]. The

temperature is kept fixed at 300 K near the outer boundary with the Langevin method. The impacting argon and  $\text{CO}_2$  clusters contain about 1000 molecules ( $\text{Ar}_{961}$ ,  $(\text{CO}_2)_{960}$ ), in accordance with the experiment [5–7], while  $(\text{O}_2)_{1440}$  and  $(\text{O}_2)_{960}$  clusters are adopted for the comparison. In addition, impacts of fictitious  $(\text{C}_3)_{960}$  clusters are also simulated in order to independently investigate the effects of oxygen and carbon atoms. The  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{C}_3$  clusters are preliminarily formed by applying Lennard-Jones potentials for the intermolecular interactions [9], but this is omitted in the impact simulation.

## 3. Results and discussions

Fig. 1 shows the time history of the number of carbon atoms emitted out of the diamond (111) surface  $N_C^{\text{out}}$  for  $\text{Ar}_{961}$ ,  $(\text{CO}_2)_{960}$ ,  $(\text{O}_2)_{1440}$  and  $(\text{C}_3)_{960}$  impacts at an acceleration energy  $E_a$  of 100 keV/cluster, where the number is defined as

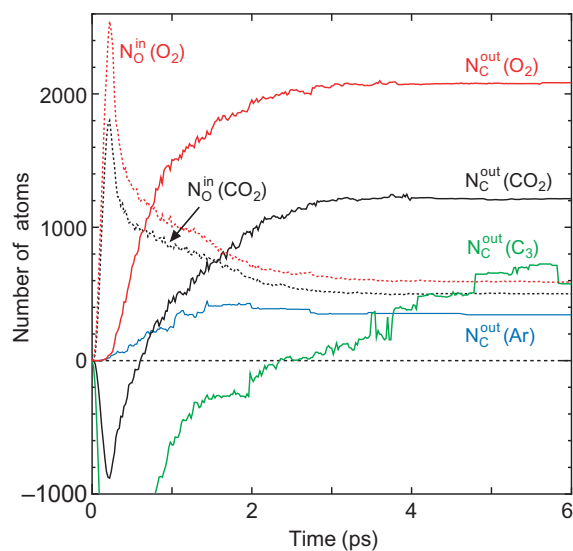


Fig. 1. Time history of the number of carbon atoms emitted from the diamond (111) surface  $N_C^{\text{out}}$  for  $\text{Ar}_{961}$ ,  $(\text{CO}_2)_{960}$ ,  $(\text{O}_2)_{1440}$  and  $(\text{C}_3)_{960}$  impacts at an acceleration energy  $E_a$  of 100 keV/cluster, where the number is defined as the offset from the initial number of the target atoms. The number of oxygen atoms staying on the diamond surface  $N_O^{\text{in}}$  is also shown for the  $\text{CO}_2$  and  $\text{O}_2$  cluster impacts.

the offset from the initial number of the target atoms. The number of oxygen atoms staying on the diamond surface  $N_O^{\text{in}}$  is also shown for the  $\text{CO}_2$  and  $\text{O}_2$  cluster impacts. A bond is determined by a cut-off length for the carbon–oxygen system in the potential functions used here, and an emitted cluster can be defined as a cluster not sharing any bond with the diamond surface. For the  $(\text{CO}_2)_{960}$  and  $(\text{C}_3)_{960}$  cluster impacts, almost all of the carbon atoms are first embedded into the diamond surface, thus  $N_C^{\text{out}}(\text{CO}_2)$  and  $N_C^{\text{out}}(\text{C}_3)$  have negative values before about 0.6 ps and 2.3 ps, respectively. However, due to the excess energy of the dissociated species, both  $N_C^{\text{out}}(\text{CO}_2)$  and  $N_C^{\text{out}}(\text{C}_3)$  result in positive values afterwards, i.e. emission instead of deposition. In addition, the final value of  $N_C^{\text{out}}(\text{C}_3)$  is apparently larger than  $N_C^{\text{out}}(\text{Ar})$ , showing that the self reactive chemical erosion using  $\text{C}_3$  clusters may also induce more emission than the simple non-reactive physical erosion using argon clusters. It should surely be noted that the result may depend much on the unsaturation of the  $\text{C}_3$  cluster which induces additional heat of reaction during the impact. Anyway, the differences in the carbon emission effect  $N_C^{\text{out}}$  among the reactive clusters  $(\text{C}_3)_{1440}$ ,  $(\text{CO}_2)_{960}$  and  $(\text{O}_2)_{1440}$  clearly exhibit the role of oxygen atoms in the reactive chemical erosion. Regarding the  $N_O^{\text{in}}$ , not a few oxygen atoms actually stay on the surface after the impact both for  $(\text{CO}_2)_{960}$  and  $(\text{O}_2)_{1440}$  clusters, however, the difference of about 80 between  $N_O^{\text{in}}(\text{CO}_2)$  and  $N_O^{\text{in}}(\text{O}_2)$  at 6 ps seems rather tiny compared to the difference in the number of impacting oxygen atoms of 960 (1920–2880). Considering that the remaining oxygen atoms stay only near the surface [13], excess oxygen atoms are easily ejected when the oxygen density near the surface is saturated. In order to evaluate the net carbon emissions and the net

atomic emissions, the values of  $N_C^{\text{out}}$  and  $N_C^{\text{out}} - N_O^{\text{in}}$  at 6 ps in Fig. 1 are summarized in Table 1. Argon atoms left in the sample will probably diffuse out eventually, hence, they are not considered here. Although the differences in the atomic emission  $N_C^{\text{out}} - N_O^{\text{in}}$  among the four cluster impacts look less pronounced than those in the carbon emission  $N_C^{\text{out}}$ , it is still clear that  $\text{O}_2$  cluster impact may have a prominent potential as an erodant. In addition, considering that the possible amount of oxygen atoms staying near the surface may easily saturate as mentioned above, the effect of remaining oxygen atoms is negligible in the case of multiple impacts with higher acceleration energy, and therefore, the net carbon atomic emission may thus rather reflect the erosion rate observed in the multiple impact experiment. In fact, the difference in the erosion ratio between argon and  $\text{CO}_2$  clusters obtained in the experiment corresponds rather well to the net carbon emission in the simulation [7–9].

Fig. 2 shows the number of emitted carbon atoms  $N_C^{\text{out}}$  as the offset from the initial value for single  $\text{Ar}_{961}$ ,  $(\text{CO}_2)_{960}$ ,  $(\text{C}_3)_{960}$  and  $(\text{O}_2)_{1440}$  cluster

Table 1

Net carbon emission  $N_C^{\text{out}}$  and net atomic emission  $N_C^{\text{out}} - N_O^{\text{in}}$  at an acceleration energy  $E_a = 100 \text{ keV}$  as the final value shown in Fig. 1

	$\text{Ar}_{961}$	$(\text{C}_3)_{960}$	$(\text{CO}_2)_{960}$	$(\text{O}_2)_{1440}$
$N_C^{\text{out}}$	344	576	1214	2084
$N_C^{\text{out}} - N_O^{\text{in}}$	344	576	713	1496

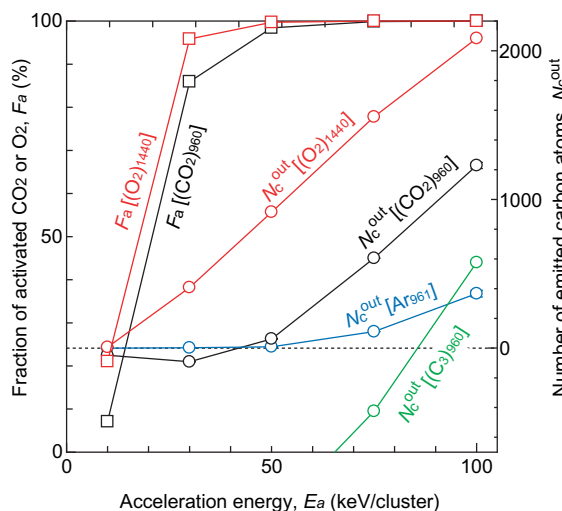


Fig. 2. Number of emitted carbon atoms  $N_C^{\text{out}}$  as the offset from the initial value for single  $\text{Ar}_{961}$ ,  $(\text{CO}_2)_{960}$ ,  $(\text{C}_3)_{960}$  and  $(\text{O}_2)_{1440}$  cluster impacts at different cluster acceleration energies  $E_a$ . The fractions of activated  $\text{CO}_2$  and  $\text{O}_2$  molecules  $F_a$ , i.e.  $\text{CO}_2$  or  $\text{O}_2$  molecules not remaining intact, are also exhibited.

impacts at different cluster acceleration energies  $E_a$ . The fractions of activated  $\text{CO}_2$  and  $\text{O}_2$  molecules  $F_a$ , i.e.  $\text{CO}_2$  or  $\text{O}_2$  molecules not remaining intact, are also exhibited. For  $\text{Ar}_{961}$  and  $(\text{CO}_2)_{960}$  cluster impacts, the emission can be strongly enhanced only with higher acceleration energy of  $E_a \geq 75 \text{ keV}$  [9]. In the case of the  $(\text{C}_3)_{960}$  impact, the impacting cluster is deposited on the surface instead of inducing emission at  $E_a \leq 75 \text{ keV}$ , indicated by negative values of  $N_C^{\text{out}}(\text{C}_3)_{960}$ . The deposition is also observed for  $(\text{CO}_2)_{960}$  at  $E_a = 30 \text{ keV}$ , where more than 80% of the impacting  $\text{CO}_2$  molecules are already dissociated and activated during the impact. Unlike these impacts, the  $(\text{O}_2)_{1440}$  cluster impact shows a remarkable erosion effect from lower acceleration energy on at 30 keV, and the effect increases almost linearly with the increase of the acceleration energy. Even at  $E_a = 100 \text{ keV}$ , where the reactive enhancement is also pronounced for the  $(\text{CO}_2)_{960}$  impact, the erosion rate of the  $(\text{O}_2)_{1440}$  impact is still 1.7 times higher than that of the  $(\text{CO}_2)_{960}$  impact. If all the available O atom would react and lead to emission, the factor should be 1.5. A factor 3 would result if only one O per  $\text{CO}_2$  would react with diamond. The difference is apparently not ascribed to the mere stability of impacting molecules because almost all of both  $\text{CO}_2$  and  $\text{O}_2$  molecules are activated at  $E_a \geq 50 \text{ keV}$ .

Fig. 3 shows a comparison of the emitted cluster size distributions between  $(\text{CO}_2)_{960}$  and  $(\text{O}_2)_{1440}$  impacts at  $E_a = 30, 50, 75$  and  $100 \text{ keV}$ . For the  $\text{O}_2$  cluster impact,  $\text{O}_2$  molecules easily take carbon atoms from the diamond surface as  $\text{CO}_2$  and  $\text{CO}$  already at 30 keV. The activated oxygen atoms react more independently as atom than as  $\text{O}_2$  molecule with carbon atoms as the acceleration energy increases, thus a prominent  $\text{CO}$  emission is observed at  $E_a = 100 \text{ keV}$ . On the other hand, impacting  $\text{CO}_2$  molecules once dissociate into  $\text{CO}$  and  $\text{O}$  and some of them may actually contribute even at a lower acceleration energy of 30 keV, but more are eventually deposited on the surface, which results in the net deposition as shown in Fig. 2. From these spectra, it is obvious that  $\text{CO}_2$  cluster impact is a kind of self irradiation using one of the two dominant products  $\text{CO}$  and  $\text{CO}_2$ , and therefore, these impacts can never surpass the  $\text{O}_2$  cluster impacts.

Although the total number of impacting atoms are the same for  $(\text{CO}_2)_{960}$  and  $(\text{O}_2)_{1440}$ , it may seem inappropriate to compare impacts with different number of molecules. The erosion effect using  $(\text{O}_2)_{960}$  is therefore examined in order to investigate the size effect in the erosion effect for  $\text{O}_2$  cluster impacts. Fig. 4 shows the numbers of emitted carbon atoms  $N_C^{\text{out}}$  at different cluster acceleration energies  $E_a$  for single  $(\text{O}_2)_{1440}$  and  $(\text{O}_2)_{960}$  cluster

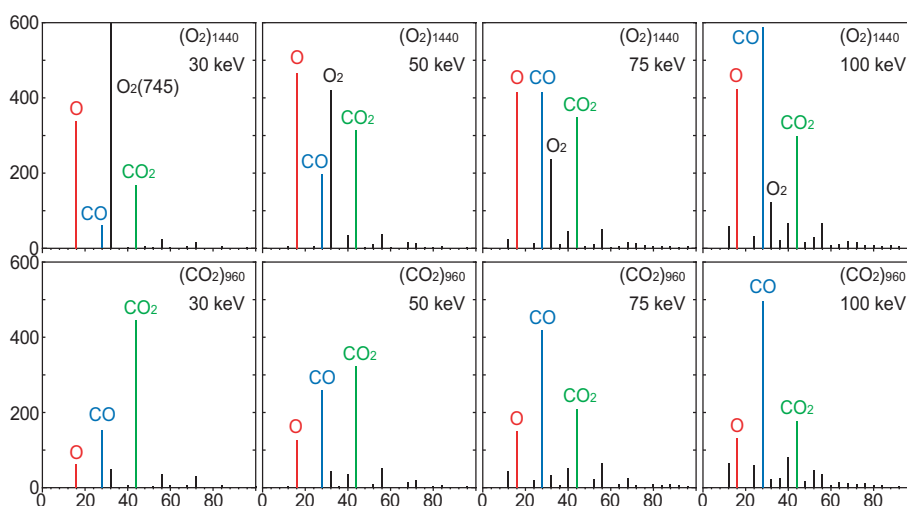


Fig. 3. Comparison of the emitted cluster size distributions between  $(\text{CO}_2)_{960}$  and  $(\text{O}_2)_{1440}$  impacts at  $E_a = 30, 50, 75$  and  $100 \text{ keV}$ .

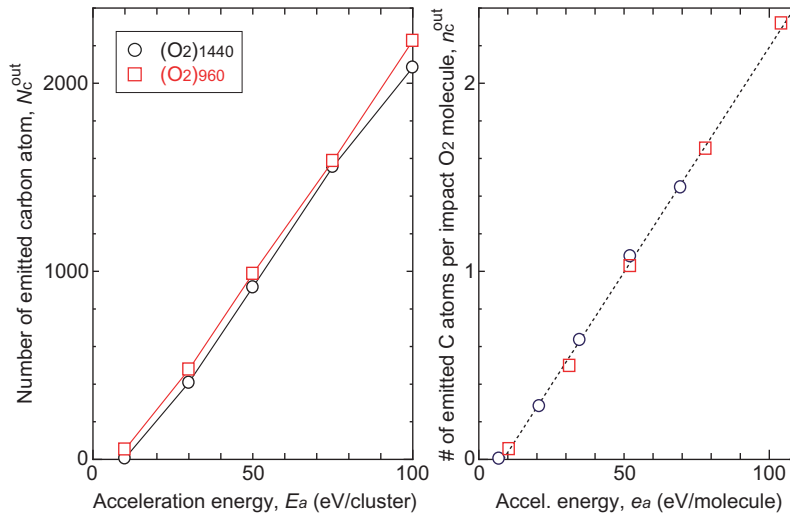


Fig. 4. Numbers of emitted carbon atoms  $N_C^{\text{out}}$  at different cluster acceleration energies  $E_a$  for single  $(O_2)_{1440}$  and  $(O_2)_{960}$  cluster impacts (left) and those normalized by the number of impacting  $O_2$  molecules as  $n_C^{\text{out}}$  and  $E_a$ , respectively (right).

impacts (left) and those normalized by the number of impacting  $O_2$  molecules as  $n_C^{\text{out}}$  and  $E_a$ , respectively (right). In the  $N_C^{\text{out}}-E_a$  diagram (left), both  $(O_2)_{960}$  and  $(O_2)_{1440}$  impacts seem to be on lines, and these are similar to the function of the volume of the plastically deformed region expressed as a linear function of the acceleration energy  $E_a$  minus a threshold energy of about 10 keV [9]. This may be explained by assuming that a certain fixed fraction of the activated ‘hot’ carbon in the deformed region reacts with the highly reactive  $O_2$  molecules and results in the emission. Except for the threshold energy, this observation is in accordance with the transient crater volume being a linear function of the impact energy [1]. Hence, the two impacts are on the same line in the  $N_C^{\text{out}}-E_a$  diagram (right) since the volume of the plastically deformed is proportional to the cluster volume, or mass, if the impact velocity is fixed.

#### 4. Conclusions

MD simulations of single argon,  $CO_2$ ,  $C_3$  and  $O_2$  cluster impacts on a diamond (111) surface are performed in order to investigate the surface erosion process. Unlike the other three impacts which only result in remarkable emission at higher

acceleration energies of  $E_a \geq 75$  keV, the  $(O_2)$  cluster impacts induce a significant effect from the lower acceleration energy  $E_a$  of 30 keV on, and the erosion rate increases almost linearly with the increase of the acceleration energy. These differences are ascribed to the reactive emission process via the production of CO and  $CO_2$  molecules. The erosion rate per molecule seems to be expressed as a linear function of the impact energy minus a threshold energy independent of the cluster size for the  $(O_2)$  cluster impacts.

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