

# PENETRATION RESISTANCE OF GRAPHENE COATED CERAMIC MATERIALS UNDER PROJECTILE IMPACTS

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**Abstract.** Extreme conditions including impact can result in material degradation, permanent damages, and occasionally property/life loss. Therefore, investigation of materials and structures under projectile impact has been a canonical field of research over the past decades. Such studies have led to the development of hybrid materials with high performance and durability under the aforementioned loading. As an emerging hybrid material, graphene oxide (GO) - silicon carbide (SiC) provides promising thermo-chemo-mechanical properties with various applications in defense, energy, and aerospace engineering. Nevertheless, penetration resistance of such composites under impact received less attention due to experimental and computational difficulties. Here, ReaxFF molecular dynamics is leveraged to address the aforesaid problem around room temperature. In that regard, the response of 4H-SiC thin films coated by GO samples under indentation and high-velocity projectile impact is studied. It is observed that (a) ceramic substrates coated by GO samples with higher functional groups concentration (oxidation degree) demonstrate softer behavior under indentation, and (b) fracture and penetration resistance under high-velocity impact are altered based on the oxidation degree of the coating layers. In essence, impact-induced complete perforation becomes more localized to the impacted region by increasing the oxidation content of the coating layers. The influence of oxygen functional groups on the adhesion energy between GO and SiC layers is also investigated. It is observed that adhesion energy between SiC and the coating can be ameliorated by the oxidation degree of the graphene samples. Eventually, the above-mentioned findings provide some insights into the bottom-up design pathways for developing ceramic-based protective barriers in which GO is used as a coating layer or reinforcement.

## 1 INTRODUCTION

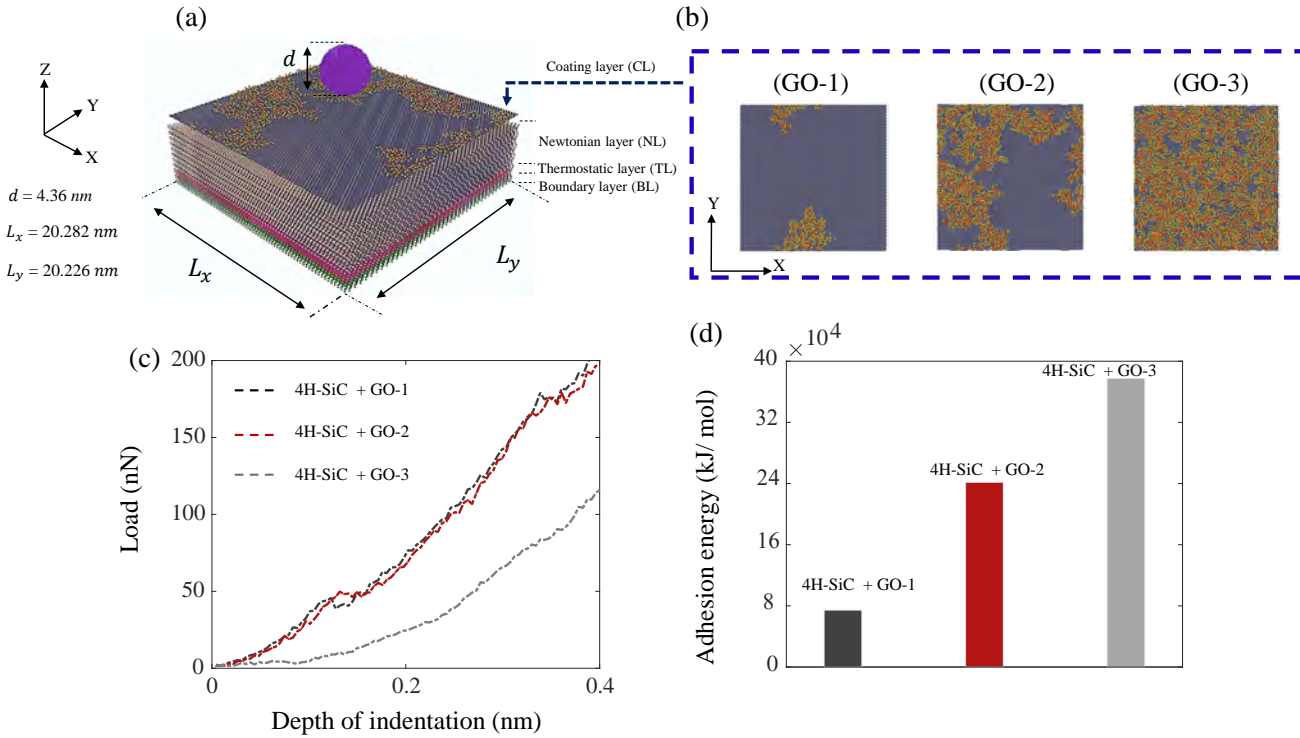
Used in various protective barriers and aerostructures, ceramics are known to possess extraordinary thermo-chemo-mechanical properties [1]. Nonetheless, the performance of ceramics is restricted by their inherent low fracture toughness and high brittleness. Retrofitting ceramics

with various reinforcing graphene-based phases can be a practical way to achieve modified ceramics with enhanced fracture properties; thus, opening new opportunities to utilize ceramics in engineering and science [2, 3].

Graphene, per se, possesses outstanding electronic, thermal, and mechanical properties [4, 5]. Therefore, it could be deduced that graphene insertion into other materials may improve the overall properties of the host materials such as ceramics. Indeed, Tian et al. [6, 7] reported that SiC thin films coated by various stacking arrangements of graphene could result in higher ballistic limit velocity under projectile impacts. Using DFT-MD simulations, Yang et al. [8] addressed the failure mechanism of graphene coated SiC during peeling test. They revealed that graphene/SiC interface failure is related to the graphene failure. Compared to graphene, graphene oxide (GO) can be more potent in terms of ameliorating interfacial interactions with a substrate and hence modifying the mechanics of penetration under projectile impacts [9]. This is attributed to the existence of oxygen-containing functional groups (or adatoms) on both sides of the basal plane of graphene. Motivated by the aforementioned feature of GO, we study GO coated SiC films under projectile impacts using ReaxFF MD [10, 11] to highlight the capacity of GO as a protective coating layer in interaction with ceramic substrates. To this aim, SiC thin films coated by GO monolayers with different oxidation degrees are deemed to characterize their response subjected to low-velocity indentation and high-velocity projectile impact; see also [11] for further details.

## 2 MODELING

Many polytypes exist for SiC due to the various stacking sequences of silicon (Si) and carbon (C) atoms. As an example, 4H-SiC is considered here to serve as the substrate for the graphene-related coatings. SiC thin substrate is established according to the orthogonal lattice structure with dimensions of  $20.282 \text{ nm} \times 20.226 \text{ nm} \times 5.5 \text{ nm}$  as illustrated in Fig.1a. Using Sinclair approach in modeling GO [12], GO monolayers of  $20 \text{ nm} \times 20 \text{ nm}$  are placed on the top face of the ceramic substrate (Fig.1b). As illustrated in Fig.1b, GO monolayers are modeled to contain various degrees of oxidation (R) which is defined as the ratio between oxygen atoms and the total number of carbon atoms (i.e.,  $R = O/C$ ). Accordingly, each GO monolayer is placed on top of the ceramic substrate (Si face (0001)) with constant separation distance of  $7 \text{ \AA}$  [11]. Once GO-SiC thin films are prepared, MD simulations (i.e., system relaxations, nanoindentation, high-velocity impact tests) are conducted in LAMMPS [13] and the pertinent results including MD trajectories are visualized leveraging OVITO [14]. For the rest of the discussions, 4H-SiC + GO-1, 4H-SiC + GO-2, and 4H-SiC + GO-3 are referred to 4H-SiC coated by the GO monolayer illustrated in Fig1.b (i.e., 4H-SiC + GO-1 means the ceramic substrate coated by the GO layer with  $R = 5 \%$ ).



**Figure 1:** (a) Indentation test of the GO coated 4H-SiC, (b) GO coating layers with different oxidation degree (GO-1: 5% oxidation, GO-2: 25% oxidation, GO-3: 50% oxidation), (c) Load - indentation curve of the GO-SiC, (d) adhesion energy comparison of the GO-SiC samples. It must be noted that the samples presented here are functionalized with hydroxyl (OH) and epoxide (O) groups on both sides of the graphene basal plane. Note that OH/O ratio for all GO coatings is set as 1. Boundary layer (BL) is a still layer while the thermostatic layer (TL) ensures the adjustment of temperature of the samples during indentation. Newtonian layer (NL) and coating layer (CL) are in direct interaction with the indenter; see also [11] for further details.

### 3 INDENTATION TEST

As depicted in Fig. 1a, nanoindentation tests are conducted on GO coated 4H-SiC films. Prior to indentation, the temperature of the GO-SiC structure is gradually raised from 1 K to room temperature over a sufficiently long period of time. This is followed by the thermal stabilization imposed by the NPT ensemble. Then, NVE ensemble is considered for a sufficiently long period of time to ensure the stability of the systems. Next, a non-atomic spherical indenter with diameter  $d$  and purely repulsive potential interaction with the samples is used for the indentation [6, 11]. As shown in Fig. 1a, thin films include three different layers: boundary layer (BL), thermostat layer (TL), and Newtonian layer (NL). Atoms in BL ( $5 \text{ \AA}$  thick) are still to eliminate the rigid body motion of the films during indentation along the  $Z$  axis. TL ( $10 \text{ \AA}$  thick) takes into account possible temperature adjustments due to the indentation process. The temperature of TL is maintained almost constant around the room temperature ( $\approx 290 - 300 \text{ K}$ ). The dynamics of NL is governed by the indentation forces generated by indenter-thin films interaction under NVE ensemble dynamics. Periodic boundary conditions along planar direction ( $X, Y$  axes), free

boundary condition along Z direction, fixed time step of 0.2 femtoseconds (fs), and an indenter's low velocity of 25 m/s are assumed for the indentation tests of all the samples.

Moreover, adhesion energy between the coating layer and the SiC film are calculated to highlight how functional groups may modify the interfacial properties of the GO-SiC layered systems. Such energy is mainly driven by the non-bonded interactions (i.e., van der Waals (vdW) and Columbic interactions). Accordingly, The adhesion energy can be expressed as [11]:

$$\Delta E = E_{total} - E_{coating} - E_{substrate}. \quad (1)$$

where  $\Delta E$ ,  $E_{total}$ ,  $E_{coating}$ ,  $E_{substrate}$  denote the interaction energy, total potential energy of the layered materials, potential energy of GO coating, and potential energy of SiC substrate respectively. For the convenience, the modulus of the adhesion energy is considered. Accordingly, the higher adhesion energy reflects the pronounced interface interaction between the coating and the SiC substrate.

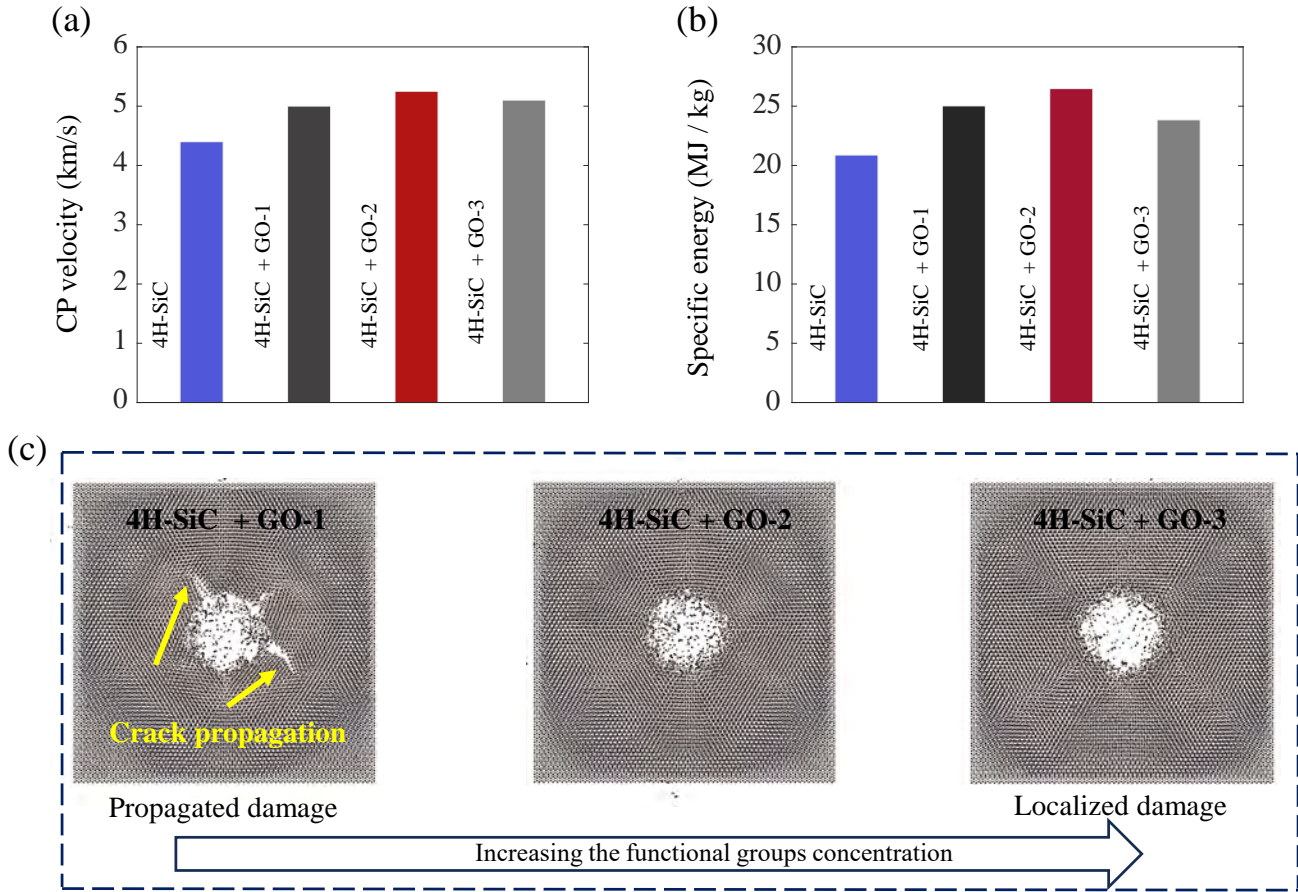
Figure 1.c-d illustrate the result of nanoindentation tests and adhesion energy of SiC coated by GO monolayers with various oxidation level. It is manifest from the plots that (a) composite film containing GO coating with the highest oxidation degree (R = 50 %) shows a noticeable softening response under nanoindentation, and (b) oxidation degree ameliorates the adhesion energy between GO and SiC. In essence, the softening behavior is attributed to the fact that introducing functional groups on the surface of graphene causes more hybrid  $sp^3$  bonds in the graphene, which are inherently weaker compared to the  $sp^2$  stiff carbon bonds of pure graphene [5]. At the same time, those functional groups enhance the adhesion of the coating with the SiC substrate.

#### 4 HIGH-VELOCITY PROJECTILE IMPACT TEST

For the ballistic impact simulation of GO-SiC structure with thickness of  $\approx 21.5 \text{ \AA}$ , NVE ensemble is imposed after the system reaches a relaxation state by an NVT ensemble [5] around the room temperature ( $\approx 290 - 300 \text{ K}$ ). It must be noted that the edges of the thin composite films is fixed to eliminate any possible rigid body motion of the system due to the high velocity projectile impact. Furthermore, the center of the projectile is placed well above the target's center to minimize any initial projectile-thin film interaction. The projectile is treated as a rigid spherical diamond ( $d= 46 \text{ \AA}$ ) with an initial velocity towards the top face of the target. Fracture patterns and penetration-resistance to the high-velocity projectile impact are assessed considering ReaxFF forcefield for all interactions, and constant time step of 0.2 fs.

In addition to the complete perforation (CP) velocity threshold, the specific penetration energy ( $E_{sp}$ ) computed at CP velocity threshold is defined to address the impact performance of the presented layered thin films.  $E_{sp}$  is expressed as [11, 15]:

$$E_{sp} = \frac{m_p V_{cp}^2}{2 \rho h \pi r_s^2}. \quad (2)$$



**Figure 2:** (a) CP velocity threshold of GO coated 4H-SiC substrates, (b) specific energy threshold of GO coated 4H-SiC substrates, (c) fracture pattern of the ceramic substrates coated by different oxidized coatings; see also [11] for further details.

where  $m_p$ ,  $V_{cp}$ ,  $\rho$ ,  $h$ ,  $r_s$  indicate the projectile's mass, CP threshold velocity, density of the thin films, thickness of the thin films, and radius of the projectile respectively. It is of note that  $h = 2.14 \text{ nm}$  is assumed for all the GO-SiC composites. Further, MD-based densities at room temperature are reported to be  $3450 \text{ kg/m}^3$ ,  $2614 \text{ kg/m}^3$ ,  $2725 \text{ kg/m}^3$ ,  $2853 \text{ kg/m}^3$  for the monolithic 4H-SiC, 4H-SiC + GO-1, 4H-SiC + GO-2, and 4H-SiC + GO-3 respectively.

Fig.2a-b show that 4H-SiC + GO-2 sample outperforms the other samples given the higher  $E_{sp}$  and CP velocity threshold. In essence, it can be deduced that the penetration-resistance of the coating layer in conjunction with the coating layer-substrate interaction govern the penetration-resistance of the SiC coated by GO. Further, various GO coating layers may result in different fracture patterns due to their intrinsic brittle to ductile transition by increasing the oxidation concentration [5, 11]. As illustrated in Fig.2c, It is evident that 4H-SiC + GO-1 sample is prone to brittle-type fracture which includes crack initiations and fragmentation [11]. As the oxidation degree increases, crack initiation is hindered for the pertinent CP velocity thresholds. This is

related to the fact that GO coating layers with higher oxidation degrees behave in a semi-ductile manner compared to the less oxidized coatings; accordingly, when they are in interaction with the brittle substrate such as 4H-SiC, the functional groups are able to impede initiations and propagation of cracks effectively in the thin films. Consequently, the fracture pattern is more confined to the impacted zone for the GO coating layers with higher oxidation concentration.

## 5 CONCLUSIONS

The performed molecular dynamics simulations offer insights into the behavior and response of 4H-SiC coated by different GO monolayers subjected to nanoindentation and high-velocity projectile impact. From the nanoindentation tests and comparing the load-indentation curves, it was observed that the GO-SiC sample with the highest oxidation level ( $R = 50\%$ ) results in a considerable softening behavior. Further, adhesion interaction between the coating layer and the substrate is enhanced as the concentration of the oxygen-containing functional groups rises. From the nanoimpact tests, it was found that while all coating layers improve the penetration-resistance of the 4H-SiC, complete perforation (CP) velocity threshold and specific penetration energy of the samples are contingent on the type of the coating layers. Furthermore, fracture pattern such as crack initiation is altered based on the oxidation degree of the coatings. In essence, GO coating layers with higher oxidation degrees inhibit the crack initiation in the thin ceramic substrate; thus, the fracture is more confined to the impacted region. This is ascribed to the ensuing adhesion feature of the oxygen-based functional groups to impede crack initiation in the thin films and induce brittle to ductile transition of the coatings. Therefore, GO-based materials could be engineered based on their oxidation content (functional groups concentration) to be employed as a protective coating layer and reinforcement for ceramic materials.

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