



# Article First-Principles Study on Graphene/Mg<sub>2</sub>Si Interface of Selective Laser Melting Graphene/Aluminum Matrix Composites

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**Abstract**: The bonding strength of a Gr/Mg<sub>2</sub>Si interface was calculated by first principles. Graphene can form a stable, completely coherent interface with Mg<sub>2</sub>Si. When the (0001)  $_{\rm Gr}/(001) _{\rm Mg_2Si}$  crystal plane is combined, the mismatch degree is 5.394%, which conforms to the two-dimensional lattice mismatch theory. At the interface between Gr/Mg<sub>2</sub>Si, chemical bonds were not formed, there was only a strong van der Waals force; the interfaces composed of three low index surfaces (001), (011) and (111) of Mg<sub>2</sub>Si and Gr (0001) have smaller interfacial adhesion work and larger interfacial energy, the interfacial energy of Gr/Mg<sub>2</sub>Si is much larger than that of  $\alpha$ -Al/Al melt and Gr/Al interfacial (0.15 J/m<sup>2</sup>, 0.16 J/m<sup>2</sup>), and the interface distance of a stable interface is larger than the bond length of a chemical bond. The interface charge density difference diagram and density of states curve show that there is only strong van der Waals force in a Gr/Mg<sub>2</sub>Si interface. Therefore, when the Gr/AlSi10Mg composite is stressed and deformed, the Gr/Mg<sub>2</sub>Si interface in the composite is easy to separate and become the crack propagation source. The Gr/Mg<sub>2</sub>Si interface should be avoided in the preparation of Gr/AlSi10Mg composite.

Keywords: first principles; selective laser melting; graphene; interface combination; Mg<sub>2</sub>Si

### 1. Introduction

As a common metal matrix composite, aluminum matrix composite has been widely used in many fields. AlSi10Mg belongs to cast Al-Si alloy, which is a kind of highperformance aluminum alloy with good casting performance and wear resistance. It is mainly used for manufacturing parts bearing a medium load [1]. With the development of science and technology, and the continuous exploration of human civilization, the existing metal materials have been unable to meet the application requirements of some high-end fields.

Researchers usually add rare earth elements into metal matrixes to strengthen materials. For example, Zhao et al. found that the plate like Mg Sn La compound can be refined, spheroidized and uniformly distributed in the Mg-3Sn-1Mn alloy with the increase of rolling reduction, and the spherical Mg Sn La compound can pin the dislocation and increase the driving force of dynamic recrystallization [2]. However, the appearance of graphene provides a new direction for the research and development of various metal matrix composites. Graphene has unique electrical, mechanical and thermal properties. It is an ideal reinforcing material for preparing light, high-strength and high-performance metal matrix composites [3]. In recent years, graphene and its derivatives have been added to the matrix materials in the form of short fibers and nanoparticles, which can improve the properties of the matrix materials.

In order to develop new aluminum matrix composites, graphene as a reinforcement phase has become a hot topic to improve the properties of aluminum-based materials [4,5].



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Shao et al. prepared graphene reinforced 5083Al composites with the pressure infiltration method. The tensile strength of graphene/5083Al was significantly enhanced compared with that of 5083Al [6]. Jeon et al. sprayed graphene aqueous solution on the surface of 5052-H32 aluminum alloy, and then prepared graphene/aluminum matrix composites through friction stir welding. The thermal conductivity of the composites increased by about 15% compared with the matrix materials, and the ductility of the composite swas improved [7]. Zhao et al. prepared TiC/graphene/graphite/Ti6Al4V composite coating with laser cladding. The composite coating contains TiC and graphene, which improves the wear resistance of the composite coating [8]. Wu et al. prepared graphene nanoflakes reinforced aluminum matrix composites through accumulative extrusion welding. Graphene nanoflakes can inhibit the local strain and improve the electrical conductivity of the composites [9].

Compared with stir casting, powder metallurgy and extrusion forming, selective laser melting (SLM) technology has many advantages. SLM can form complex structural parts at one time, which plays a role in reducing the manufacturing cost. The solidification speed of metal materials in the SLM forming process is very fast, which greatly limits the growth of metal material grains, and can produce high-performance metal parts with ultra-fine grains [3]. Zhang et al. prepared Ti/Al-Cu-Mg alloy with SLM technology. The addition of Ti can effectively inhibit the generation of cracks, promote the grain refinement of Al-Cu-Mg alloy and greatly improve the mechanical properties of the alloy [10].

The mechanical properties of Gr/AlSi10Mg composites formed by SLM are better than those of aluminum matrix composites formed by traditional processes. Wu et al. prepared graphene nanoflakes reinforced AlSi10Mg composites with selective laser melting technology. The friction resistance of the composites was reduced, and the wear resistance was greatly improved [11]. Zhao et al. modified the surface of graphene nanosheets with the chemical reduction method, and then prepared graphene reinforced AlSi10Mg composites with SLM technology. Graphene played a role in promoting nucleation and pinning dislocation in the composites [12]. However, there are also some problems. For example, Zhao et al. prepared carbon/AlSi10Mg composites with SLM technology, which cannot avoid the existence of spherical voids in the manufacturing process [13]. The graphene added into the AlSi10Mg and the matrix materials form a variety of heterogeneous interfaces, which can easily become a source of crack propagation, so that the composites are accompanied with significant potential risks in use, so it is necessary to study the bonding strength of these interfaces. The first principle can predict the interface between the second phase and the matrix. Zhuo et al. used the first principles density functional theory to study the possibility of nucleation of aluminum atoms on the surface of NbB<sub>2</sub>. The Al/NbB<sub>2</sub> nucleation interface is stable, and  $\alpha$ -Al can nucleate and grow on NbB<sub>2</sub> (0001) [14]. Liu et al. calculated the interfacial adhesion work, charge density difference, energy band structure and density of states curve of pure Gr and Gr doped Al (111)/Gr/Al (111) and Al (111)/Gr/Al (111) interfaces through first principles. The results show that the bonding strength of the Al (111)/Gr/Al (111) interface can be increased by more than ten times by doping Gr [15]. Li et al. studied the atomic structure, bonding and interface energy of the  $Mg/Al_4C_3$  interface based on first principles calculation. The interface energy of Mg/Al<sub>4</sub>C<sub>3</sub> interface is smaller than that between  $\alpha$ -Mg and magnesium melt. Al<sub>4</sub>C<sub>3</sub> particles have excellent heteromorphic nucleation ability for  $\alpha$ -Mg grains [16].

However, the mismatch and bonding strength between Gr/Mg<sub>2</sub>Si interfaces are rarely reported and studied, so the first principles method is used to study the Gr/Mg<sub>2</sub>Si interface. Three representative low index surfaces, (001), (011) and (111) of Mg<sub>2</sub>Si, were selected to establish heterogeneous interfaces with Gr (0001), respectively. The interfacial bonding strength, interfacial electron distribution and bonding of the three interfaces were calculated. The calculated interfacial energy was compared with that of  $\alpha$ -Al/Al melt, and its effect on crack propagation was analyzed.

# 2. Calculation

The convergence test and structural stability calculation of the surface model and interface model were completed by the CASTEP module of Materials Studio software. In this module, the self-consistent field method (SCF) is used to solve the Kohn–Sham equation of the multiparticle system, and the ground state energy of the multiparticle system is obtained [17]. The convergence threshold of the self-consistent field calculation in simulation calculation is set to  $5.0 \times 10^{-7}$  eV/atom. In the CASTEP module, the BFGS (Broyden Fletcher Goldfarb Shanno) algorithm is used to optimize the total energy of the multi particle system, and then the stable model with the lowest energy is obtained [18]. The Generalized Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) potential function is used in the simulation, the cutoff energy of Gr/Mg<sub>2</sub>Si interface is 620 eV, the vacuum layer with thickness of 10 Å is used to establish the model and the k-point grid is selected (9 × 9 × 1).

#### 3. Results and Discussion

Gr/AlSi10Mg composites containing 0.15 wt% GR were fabricated by SLM. It can be seen from the XRD patterns of AlSi10Mg material Al and Gr/AlSi10Mg composite in Figure 1 that there are Al, Si and Mg<sub>2</sub>Si in AlSi10Mg formed by SLM, and these three phases exist in the same sample of Gr/AlSi10Mg composite. Zhao et al. used SLM technology to form Gr/AlSi10Mg composites containing 0.15 wt% Gr. SEM analysis showed that graphene did not agglomerate in the composites and dispersed evenly. The first principles calculation showed that there was a mixture of covalent bonds and ionic bonds on the Gr (0001)/Al<sub>4</sub>C<sub>3</sub> (0001) interface, and it was found that the carbon end was easier to alloy the interface between GR and Al<sub>4</sub>C<sub>3</sub> [19]. The Mg<sub>2</sub>Si/Gr interface is formed in the composite material due to the random distribution of graphene in the composite material. The stability of this interface has a certain influence on the performance of the composite material, so it is necessary to calculate the interface bonding strength.



Figure 1. XRD patterns of SLM-formed AlSi10Mg and Gr/AlSi10Mg Composites.

#### 3.1. Gr/Mg<sub>2</sub>Si Interface Mismatch Degree

Figure 2 is a schematic diagram of the orientation relationship of the  $Gr/Mg_2Si$  matching crystal plane. There is a certain atomic arrangement gap between Gr and  $Mg_2Si$ . The Bramfitt two-dimensional lattice mismatch model is used to calculate the lattice mismatch of  $Gr/Mg_2Si$  interface.



Figure 2. The potential orientation relationship between Gr and Mg<sub>2</sub>Si.

The formula of the Bramfitt two-dimensional lattice mismatch model is [20]:

$$\delta_{(hkl)_{n}}^{(hkl)_{s}} = \sum_{i=1}^{3} \frac{\frac{\left|d_{[uvw]_{s}^{i}}\cos\theta - d_{[uvw]_{n}^{i}}\right|}{d_{[uvw]_{n}^{i}}}}{3} \times 100\%$$
(1)

where  $(hkl)_s$  is the low index crystal plane of Gr substrate;  $[uvw]_s$  is the low index crystal direction on the  $(hkl)_s$  crystal plane;  $(hkl)_n$  is the low index crystal plane of Mg<sub>2</sub>Si substrate;  $[uvw]_n$  is the low index crystal direction on the  $(hkl)_n$  crystal plane;  $d_{[uvw]_s}$  and  $d_{[uvw]_n}$  are the lattice spacing along the  $[uvw]_s$  and  $[uvw]_n$  crystal directions respectively;  $\theta$  is the angle between  $[uvw]_s$  and  $[uvw]_n$ .

According to the two-dimensional lattice mismatch theory, a core with  $\delta$  less than 6% is an effective nucleation core, which can realize one-to-one correspondence between atoms on both sides of the interface. This kind of interface is called a fully coherent interface; a core with  $\delta = 6 \sim 15\%$  is a medium effective nucleation core, which may form semi coherent interface; when  $\delta$  is more than 15%, the interface type belongs to non-coherent interface, which cannot be used as a heterogeneous nucleation substrate of nucleating material.

Table 1 shows the specific facet index, orientation index, offset angle and calculated lattice mismatch under the three matching methods in Figure 2. When the (0001) plane of graphene is combined with the (001) plane of Mg<sub>2</sub>Si, the lattice mismatch is 5.394%, which indicates that the atoms on both sides of the interface are one-to-one corresponding, forming a fully coherent interface with low interface energy. For (0001)  $_{\rm Gr}/(111) _{\rm Mg_2Si}$  orientation, the lattice mismatch degree belongs to the range of medium effective nucleation and can form a semi-coherent interface. For (0001)  $_{\rm Gr}/(011) _{\rm Mg_2Si}$  orientation, the lattice mismatch degree between the two materials reaches 15.340%, and the interface bonding mode is incoherent interface. In conclusion, a stable interface structure can be formed between graphene and Mg<sub>2</sub>Si under the specific matching orientation.

### 3.2. Gr/Mg<sub>2</sub>Si Interfacial Bonding Strength

Three Mg<sub>2</sub>Si/Gr interface models, Mg<sub>2</sub>Si (001)/Gr (0001), Mg<sub>2</sub>Si (011)/Gr (0001) and Mg<sub>2</sub>Si (111)/Gr (0001), were established. The interfacial adhesion work, interfacial energy and interfacial charge distribution of these three interface structures were calculated and analyzed, and the stability of the Mg<sub>2</sub>Si/Gr interface was discussed.

Parameter	(0001) <sub>Gr</sub> /(001) <sub>Mg2Si</sub>			(0001) <sub>Gr</sub> /(011) <sub>Mg2Si</sub>			(0001) <sub>Gr</sub> /(111) <sub>Mg<sub>2</sub>Si</sub>		
[uvtw] <sub>Gr</sub>	[1120]	[3300]	[4220]	[1120]	[3300]	[4220]	[1120]	$[2\overline{11}0]$	[1210]
[uvw] <sub>Mg2Si</sub>	[100]	[010]	[110]	[001]	$[1\overline{1}0]$	$[1\overline{1}1]$	$[10\overline{1}]$	$[01\overline{1}]$	$[11\overline{2}]$
d[uvtw] <sub>Gr</sub>	4.261	4.92	6.509	4.261	4.92	6.509	4.920	4.920	4.920
d[uvw] <sub>Mg2Si</sub>	4.519	4.519	6.391	4.519	6.391	7.827	4.519	4.519	4.519
θ	0	0	4	0	0	6	0	0	0
δ		5.394%			15.340%			8.874%	

Table 1. The matching parameters of potential crystallographic orientation relationship between Gr and Mg<sub>2</sub>Si.

The interfacial adhesion work of the Mg<sub>2</sub>Si/Gr interface is calculated as follows [21,22]:

$$W_{ad} = \frac{1}{A} \left( E_{total}^{Gr} + E_{total}^{Mg_2Si} - E_{total}^{Gr/Mg_2Si} \right)$$
(2)

where  $E_{total}^{Gr}$ ,  $E_{total}^{Mg_2Si}$  and  $E_{total}^{Gr/Mg_2Si}$  are the total energy of the surface model and the interface model; A is the area of the interface model.

The interface energy of Mg<sub>2</sub>Si/Gr interface structure can be calculated by the following formula [23,24]:

$$E_{Mg_{2}Si} = \frac{1}{A} \left[ E_{slab} - N_{Si} \mu_{Mg_{2}Si}^{bulk} + (2N_{Si} - N_{Mg}) \mu_{Mg} - N_{C} \mu_{C}^{bulk} \right] - \delta_{Mg_{2}Si} - \delta_{Gr}$$
(3)

where  $E_{Mg_2Si}$  is the total energy of the Mg<sub>2</sub>Si/Gr interface model;  $N_{Mg}$  and  $N_{Si}$  are the number of magnesium and silicon atoms in Mg<sub>2</sub>Si surface model;  $N_c$  is the number of carbon atoms in graphene surface model;  $\mu_C^{bulk}$  is the chemical potential of a single carbon atom in the graphene surface model;  $\delta_{Mg_2Si}$  and  $\delta_{Gr}$  are the surface energies of Mg<sub>2</sub>Si and Gr surface models respectively.

#### 3.2.1. Mg<sub>2</sub>Si (001)/Gr (0001) Interfacial Bonding Strength

According to the convergence test of the Mg<sub>2</sub>Si (001) surface model, there are two kinds of Mg<sub>2</sub>Si (001) surface models used to establish the interface structure, which are seven-layer Mg-termination surface and nine-layer Si-termination surface. Because there are two different atomic arrangements in the first layer of the nine-layer Si-termination surface, three Mg<sub>2</sub>Si (001)/Gr (0001) interface models in Figure 3, Mg-termination, Si-termination center-sited and Si-termination top-sited, are established according to the relative positions of the interface atoms.



**Figure 3.** Interfacial atom stacking site and interfacial model of Mg<sub>2</sub>Si (001)/Gr (0001) interface: (a) Mg-termination; (b) Si-termination-center-sited; (c) Si-termination-top-sited (the green ball represents Mg atom, the yellow ball represents Si atom, the gray ball represents C atom).

After structural relaxation, the interface model is in the lowest energy state, and the interfacial adhesion work of the interface structure is shown in Table 2. The data in Table 2 show that the interfacial adhesion work of the Si-termination-top-sited interface is the largest, which is  $1.187 \text{ J/m}^2$ , while that of the other two interface models is relatively small. From the optimized interface spacing in the table, it is found that the interface spacing of the three interface models is still large after structure optimization, which indicates that the stability of the Mg<sub>2</sub>Si (001)/Gr (0001) interface model is poor. The distance of the chemical bond is usually less than 2.6 Å, the distance of the hydrogen bond is in the range of 2.6~3.1 Å and the distance of the strong van der Waals interaction is  $3.1\sim5.0$  Å [25]. According to the data in Table 2, the stable interface spacing of Mg-termination interface is 4.31 Å, which reaches the distance of strong van der Waals action. According to the bond length, the strong van der Waals bond is formed at the interface of Mg<sub>2</sub>Si (001)/Gr (0001) three models.

**Table 2.** The interfacial spacing of complete relaxation of  $Mg_2Si$  (001)/Gr (0001) interfaces and the corresponding work of adhesion and interfacial energy.

Interface	Stacking	d <sub>0</sub> (Å)	Wad (J/m <sup>2</sup> )	γint, Mg-Rich (J/m <sup>2</sup> )	γint, Mg-Poor (J/m <sup>2</sup> )
Mg-termination	-	4.31	0.109	1.451	3.814
	Center-sited	3.80	0.422	5.495	3.169
Si-termination	Top-sited	3.80	1.187	5.494	3.168

The interface energy of the Mg<sub>2</sub>Si (001)/Gr (0001) interface model can be calculated by Equation (3). The calculated interface energy results are shown in Table 2. The interface energy of the Si-termination interface is larger than that of Mg-termination interface, and the combination of magnesium atoms and graphene at the interface is more conducive to the formation of a stable interface structure. At the same time, it is found that the interface energy of the three kinds of interface is relatively large, the maximum value is 5.495 J/m<sup>2</sup>, which is much larger than that of  $\alpha$ -Al/Al melt and Gr/Al interfacial (0.15 J/m<sup>2</sup>, -0.16 J/m<sup>2</sup>) [14,26]. The higher the interfacial energy is, the worse the stability of the interface structure is. Therefore, when the binding orientation between Mg<sub>2</sub>Si and graphene is Mg<sub>2</sub>Si (001)/Gr (0001), the stability of the interface structure is poor.

Figure 4 shows the charge differential density diagram of three  $Mg_2Si$  (001)/Gr (0001) interfaces. In the three interface models, there is a strong interaction between the carbon atoms of graphene, and there are directional charge accumulation regions around each carbon atom. The existence of these charge accumulation regions makes the regular hexagonal carbon atom grid of graphene very stable. It can be seen from Figure 4 that there are wide gap regions at the three interfaces, and there is no chemical bond between the atoms on the  $Mg_2Si$  (001) surface and the carbon atoms of the  $Mg_2Si$  (001) surface. There are directional charge regions around the interface atoms of the  $Mg_2Si$  (001) surface in the three interface models. The charge around the interface Mg atom in Figure 4a tends to transfer to graphene. This phenomenon can also be observed in Figure 4b,c. It shows that there are weak interaction forces between the  $Mg_2Si$  (001) surface and the Gr (0001) surface in the three models, and these forces can improve the interfacial bonding strength of  $Mg_2Si$  (001)/Gr (0001) to a certain extent.

Figure 5 shows the partial-wave state density curves of three Mg<sub>2</sub>Si (001)/Gr (0001) interfaces. Figure 5a shows the partial-wave state density curve of the Mg-termination interface structure. The charge orbit of the nearest Mg atom from graphene changes greatly compared with that of the inner Mg atom. A new peak appears on the P orbit of the 1st Mg atom near the Fermi level; there is no peak value of carbon atoms in graphene near the same charge level, which indicates that there is no hybridization between the charge orbitals of carbon atoms and magnesium atoms, only mutual attraction, which is consistent with the analysis results of the charge differential density diagram. Figure 5b,c are the partial-wave state density curves of Si-termination interface structures of two different end

atoms, the results show that the partial-wave state density curves of interface mg and Si atoms are very close. Compared with inner Mg atoms, the s and p orbitals of interface Mg atoms are smoother and the number of peaks is less. There is only one large peak between  $5 e \sim 0 V$  for interface Si atoms, while there are two adjacent large peaks between  $5 e \sim 0 V$  for inner Si atoms, which indicates the location of interface Si atoms and inner Si atoms. However, there is no overlap or hybridization in the partial-wave state density curves of the two Si-termination interface structures, so no chemical bond is formed at the interface.



**Figure 4.** The charge density difference diagram for Mg<sub>2</sub>Si (001)/Gr (0001) interfaces: (**a**) Mg-termination; (**b**) Si-termination-center-sited; (**c**) Si-termination-top-sited.

#### 3.2.2. Mg<sub>2</sub>Si (011)/Gr (0001) Interfacial Bonding Strength

Figure 6 shows two interface models of  $Mg_2Si$  (011)/Gr (0001): Si center-sited and Mg center-sited. The  $Mg_2Si$  (011) surface model was placed above the Gr (0001) surface model when the interface model was established. According to the convergence test, the  $Mg_2Si$  (011)/Gr (0001) interface structure was constructed by selecting five-layer Si center-sited, Mg center-sited surface models and Gr (0001) surface.

After structural relaxation, the calculated stable interfacial spacing and interfacial adhesion work of the Mg<sub>2</sub>Si (011)/Gr (0001) interface are shown in Table 3. The results show that the interface spacing of the two models are 4.010 Å and 3.873 Å, respectively. The interface spacing is large, and there is van der Waals force at the interface. Moreover, the interfacial adhesion work of the two models is negative. It is concluded that the stability of the Mg<sub>2</sub>Si (011)/Gr (0001) interface is poor.

**Table 3.** The interfacial spacing of complete relaxation of  $Mg_2Si$  (011)/Gr (0001) interfaces and the corresponding work of adhesion and interfacial energy.

Interface	d <sub>0</sub> (Å)	Wad (J/m <sup>2</sup> )	γint, Mg-Rich (J/m <sup>2</sup> )	γint, Mg-Poor (J/m <sup>2</sup> )
Si-center-sited	4.010	-1.449	5.339	5.339
Mg-center-sited	3.873	-1.456	5.337	5.337

The interface energy of the Mg<sub>2</sub>Si (011)/Gr (0001) interface model is calculated by Equation (3). The results are shown in Table 3. The interface energy of the two interfaces is much larger than that of the  $\alpha$ -Al/Al melt and Gr/Al interfacial (0.15 J/m<sup>2</sup>, -0.16 J/m<sup>2</sup>), which indicates that when the Mg<sub>2</sub>Si (011) surface is combined with the Gr (0001) surface, the interface stability is poor, the bonding strength is low and the interface separation occurs easily. The difference in interface energy between the two interfaces is small, which indicates that the type of end atoms on the Mg<sub>2</sub>Si (011) surface has little effect on the

interface structure in the Mg<sub>2</sub>Si (011)/Gr (0001) interface. As shown in Figure 7, there is obvious interaction between carbon atoms in graphene in the two Mg<sub>2</sub>Si (011)/Gr (0001) interfaces, the charge distribution around carbon atoms has obvious directionality and there is a strong charge accumulation region between adjacent carbon atoms, which makes graphene structure have strong stability.



**Figure 5.** Partial density of states for Mg<sub>2</sub>Si (001)/Gr (0001) interfaces: (**a**) Mg-termination; (**b**) Sitermination-center-sited; (**c**) Sitermination-top-sited.

In Figure 7, there is also a gap between the graphene and the Mg<sub>2</sub>Si in the Mg<sub>2</sub>Si (011)/Gr (0001) interface model, but the width is reduced, which indicates that the interaction strength between the two surface models is enhanced. However, because there is no charge transfer phenomenon in the two interface models, no chemical bond is formed. It can be seen from Figure 7a that the charge distribution around the surface silicon atoms in the Si-center-sited interface has a certain directionality, and the charge transfer trend from

silicon atoms to graphene is obvious. Because of the large interface spacing, there is no charge transfer between them. The two surface Mg atoms in the Mg-center-sited interface also forms a low charge region on the side close to the graphene, and the distance between the low charge region of graphene and Mg<sub>2</sub>Si in the Mg-center-sited interface is relatively close, which leads to the enhancement of the bonding strength between them.



**Figure 6.** Interfacial atom stacking site and interfacial model of  $Mg_2Si$  (011)/Gr (0001) interface: (a) Si-center-sited; (b) Mg-center-sited (the green ball represents Mg atom, the yellow ball represents Si atom, the gray ball represents C atom).



**Figure 7.** The charge density difference diagram for Mg<sub>2</sub>Si (011)/Gr (0001) interfaces: (**a**) Si-center-sited; (**b**) Mg-center-sited.

Figure 8 shows the partial-wave state density curves of two Mg<sub>2</sub>Si (011)/Gr (0001) interfaces. Figure 8a shows the partial-wave state density curve of the Si-center-sited interface structure. Compared with the charge orbit of the inner silicon atom, the charge orbit of the interface silicon atom changes obviously under the influence of graphene. The peaks of the S and P orbitals of the first carbon atom are greatly enhanced, and the number of peaks of P orbitals of the first carbon atom decreases near Fermi level, which indicates that the first carbon atom is different from graphite, and that there is a strong interaction between the carbon atoms in alkenes; however, because there is no orbital hybridization between them, no chemical bond is formed at the interface. Figure 8b shows the partial-wave state density curve of the Mg-center-sited interface structure. Compared with the charge orbit of the inner Mg atom, the results show that there are some new and

smaller peaks in the charge orbit of the first Mg atom between 5 ev~10 ev, and the peaks at other positions have also changed, which indicates that there is interaction force between the first magnesium atom and the carbon atom in graphene, but there is no obvious orbital resonance between them, therefore there is no chemical bond at the interface.

# 3.2.3. Mg<sub>2</sub>Si (111)/Gr (0001) Interfacial Bonding Strength

Figure 9 shows the interface model and atomic stacking position of the Mg<sub>2</sub>Si (111)/Gr (0001) interface. According to the convergence test of the surface model, 8 layers of Mg-termination surface and 10 layers of Si-termination surface and Gr (0001) surface were selected to construct the Mg<sub>2</sub>Si (111)/Gr (0001) interface structure. The Gr (0001) surface model is above the Mg<sub>2</sub>Si (111) surface model. In this simulation, two kinds of interface models with different kinds of end atoms are constructed: Mg-termination and Si-termination.



Figure 8. Partial density of states for  $Mg_2Si$  (011)/Gr (0001) interfaces: (a) Si-center-sited; (b) Mg-center-sited.



**Figure 9.** Interfacial atom stacking site and interfacial model of  $Mg_2Si$  (111)/Gr (0001) interface: (a) Mg-termination; (b) Si-termination (the green ball represents Mg atom, the yellow ball represents Si atom, the gray ball represents C atom).

The data in Table 4 are the interfacial adhesion work of the two Mg<sub>2</sub>Si (111)/Gr (0001) interfaces after structural optimization. According to the bond length classification, it is judged that there is a strong van der Waals force at the Mg<sub>2</sub>Si (111)/Gr (0001) interface. Comparing the strength of the two interfaces, it is found that the Mg-termination interface has smaller stable interface spacing and larger interfacial adhesion work, and its stability is higher than that of the Si-termination interface.

**Table 4.** The interfacial spacing of complete relaxation of  $Mg_2Si$  (111)/Gr (0001) interfaces and the corresponding work of adhesion and interfacial energy.

Interface	d <sub>0</sub> (Å)	Wad (J/m <sup>2</sup> )	γint, Mg-Rich (J/m <sup>2</sup> )	γint, Mg-Poor (J/m <sup>2</sup> )
Mg-termination	3.708	0.0286	4.32	6.68
Si-termination	4.024	0.0158	8.35	5.97

According to Equation (3), the change of interface energy of two Mg<sub>2</sub>Si (111)/Gr (0001) interfaces in the range of  $\Delta \mu_{Mg}$  is shown in Table 4. The interfacial energy of the Mg-termination interface is 4.32~6.68 J/m<sup>2</sup>, and that of Si-termination interface is 5.97~8.35 J/m<sup>2</sup>. The interfacial energy of both interfaces is relatively large, which is not conducive to the formation of stable interface structure.

Figure 10a shows the charge differential density diagram of the Mg-termination interface. There is a strong charge accumulation region between carbon atoms in graphene, which indicates that the carbon atoms in graphene have charge transfer and form a strong covalent bond. The distance between the Mg layer and the graphene layer is large, and the charge distribution around the Mg atom is almost circular, which indicates that the graphene layer has little influence on the Mg atom at the interface, and the interaction between Mg<sub>2</sub>Si and graphene in the Mg-termination interface is small. Figure 10b shows the charge differential density diagram of the Si-termination interface. In Figure 10b, there is also a strong charge accumulation area between the carbon atoms in graphene. The difference is that the silicon atom layer combined with graphene has obvious regionalization characteristics, and the charge around silicon atom shows a trend of transferring to one side of the graphene, indicating that there is a force between the graphene and silicon atom layers.



**Figure 10.** The charge density difference diagram for  $Mg_2Si$  (111)/Gr (0001) interfaces: (a) Mg-termination; (b) Si-termination.

Figure 11 shows the partial density of states of two Mg<sub>2</sub>Si (111)/Gr (0001) interfaces. Figure 11a shows the partial-wave state density curve of graphene and Mg<sub>2</sub>Si atoms in the Mg-termination interface. Comparing the partial-wave state density curve of magnesium atoms in different layers, the density of states curves of two layers of magnesium atoms near the interface have changed greatly. Due to the influence of graphene, the density of states curve of the first Mg atom is obviously different from that of fourth and fifth Mg atoms. In the vicinity of -2 eV, a new peak appears in the P orbital of the first Mg atom, but there is no orbital hybridization between the electronic orbitals of Mg and C atoms; only the peak increases, so there is no chemical bond between them. Combined with the above analysis, it is judged that there is a strong van der Waals force in the Mg-termination interface.

Figure 11b shows the partial-wave state density curves of graphene and Mg<sub>2</sub>Si atoms at the Si-termination interface. Compared with the inner silicon atom, the partial density of states of the first silicon atom changes greatly. Besides, the peak value of the first silicon atom near -8 eV becomes higher. In addition, a high isolated peak is formed near -1 eV instead of a continuous peak such as the inner silicon atoms. According to these phenomena, it is found that there is interaction between carbon atoms in graphene and silicon atoms in Mg<sub>2</sub>Si, and the peak values of the first silicon atoms and carbon atoms, but there is no orbital hybridization between silicon atoms and carbon atoms. Therefore, there is no chemical bond between the surface of graphene and the surface of Mg<sub>2</sub>Si in a Si-termination interface, only van der Waals force exists. Combined with the above analysis, it can be concluded that the force in a mg-termination interface is stronger than that in a Si-termination interface.



**Figure 11.** Partial density of states for Mg<sub>2</sub>Si (111)/Gr (0001) interfaces: (**a**) Mg-termination; (**b**) Si-termination.

#### 4. Conclusions

- (1). According to the calculation results of the Bramfitt two-dimensional lattice mismatch model, the  $Gr/Mg_2Si$  matching model has a small lattice mismatch under the specific interface orientation, which can form a stable two-phase interface, indicating that graphene can form a stable interface with  $Mg_2Si$ .
- (2). The results of the interface stability calculation of Mg<sub>2</sub>Si/Gr show that the three kinds of Mg<sub>2</sub>Si/Gr interface have smaller interfacial adhesion work, larger stable interface spacing and larger interface energy, which are not conducive to the formation of stable interface structure. The results of the charge differential density analysis show that there is no charge transfer between the interface atoms in the Mg<sub>2</sub>Si/Gr interface, and there is no chemical bond between the Mg<sub>2</sub>Si surface and the Gr surface. The partial-wave state density curve of the interface atom shows that the partial charge orbit of the interface atom has changed, indicating that, although there is no chemical bond at the interface, there is a strong van der Waals force at the Mg<sub>2</sub>Si/Gr interface.
- (3). According to the analysis results of the Mg<sub>2</sub>Si/Gr interface stability, the interface energy of Mg<sub>2</sub>Si/Gr is much higher than that of  $\alpha$ -Al/Al melt (0.15 J/m<sup>2</sup>), no chemical bond is formed at the interface and the Mg<sub>2</sub>Si surface and Gr surface only rely on physical adsorption. When the Gr/AlSi10Mg composite is deformed by the applied load, the Mg<sub>2</sub>Si/Gr interface can easily separate and become a crack propagation source. Therefore, the interface between Mg<sub>2</sub>Si and Gr should be avoided as much as possible in the preparation of Gr/AlSi10Mg composite.

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