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DFT calculations of polymer/gold substrate adhesion in wafer fabrication

PING WU, HONG MEI JIN, HONG LIN LIU
Institute of High Performance Computing, 1 Science Park Road, #01-01 The Capricorn, Singapore Science Park II, Singapore 117528
E-mail: wuping@ihpc.nus.edu.sg

By a density functional method, the adhesion characteristics of polymer/Au with and without impurities are investigated. A slab model is employed to study the importance of different crystal faces. Results showed that in general the adhesion between the polymer and Au substrate is weak, regardless of any crystal faces. But the adhesion between polymer and Au(100) face is relatively stronger comparing with another two faces. Through geometry optimisation of polymer on Au(111), the effects of impurities including C, O, Si, NaOH and H_2O are analysed. Results showed that the majority of the impurities are harmful for the adhesion, especially H_2O and NaOH, which should be removed during wafer fabrication process. © *2003 Kluwer Academic Publishers*

1. Introduction

Poor interfacial adhesion of photo-resist polymer and gold substrate has been for long a problem in the wafer fabrication due to the intrinsic properties of gold. It is responsible for many device failures observed in the industry. To solve the problem, many methods such as modification of gold surfaces by thermal graft copolymerization [1] have been used, however, none of them show great improvement. The purpose of this study is to explore a theoretical understanding of the adhesion mechanism, which is still lacking at the moment but might be useful for the further improvement of adhesion. To this end, we started with the morphology importance (MI) study of crystal Au by using BFDH (Bravais-Friedel-Donnay-Harker) law. Theoretically, a bulk crystal may possess an infinite number of faces. However, practically grown crystals possess a limited number of faces which are the slowest growing faces and morphologically important. To correlate the morphological development of crystals with their internal structure, Bravais and Friedel established the Bravais-Friedel law [2, 3] which claims that the larger the interplanar distance, the more important the corresponding crystal face. Later Donnay and Harker [4] found that this law is sometimes violated. So, they extended this law by considering the screw axis and the glide planes and established BFDH law. The BFDH law often gives satisfactory description of the morphology of the crystals. But it still has some drawbacks due to its purely geometrical consideration. Therefore, in this study, density functional theory (DFT) calculation is further performed based on the results obtained from BFDH law. The objective of the DFT calculation is first to identify the most possible growing Au faces, then, geometry optimisation of polymer/substrate interface is performed to compare the adhesion strength of the selected faces. In addition, Au(111) is used, as an example, to further investigate the impurity effects on adhesion.

2. Computational details

2.1. Determine the important crystal faces

The shape of a crystal is determined by the relative rates of atomic particle deposition on its various faces. The general rule is that the faces, which grow slowly, appear as large developed faces and are important. In this study, the important faces are screened out by using BFDH law, which is a quick method to identify the morphology importance according to geometry configuration. The top three important faces are selected to perform more expensive DFT calculations. Since a crystal face might be described by a corresponding slice, the energy calculation for three faces will be carried out with slab-DFT method. The slab model contains the total number of atoms in the unit cell and a vacuum layer as high as 1 nm. The main advantage of this geometry is that the density function equation can be used exactly as for a bulk crystalline materials, if the vacuum is adequate to avoid the interaction between the slabs. The slice energy is obtained by subtracting the sum of the isolated atomic energy E_a from the total energy of slab E_{slab}

$$E_{\text{slice}} = E_{\text{slab}} - \sum_a E_a \tag{1}$$

The standard DFT software Dmol3, which has been successfully applied to band structure calculations of insulating and metallic solid [5–7], is employed to calculate the slab energy. To make the results comparable, the calculation parameters are kept the same for all slabs as following: non-local DFT with gradient corrected exchange potential and correlation potential [8], double-numerical valence functions (basis set cut-off 11.0 a.u.) with effective core potentials [9], octupole function fitting density for the integration calculations, the SCF convergence (1.0E-05 Hartree) and the atomic charge defined by Hirshfeld [10].

2.2. Adhesion energy calculation

To obtain adhesion energy, geometry optimisation of polymer on top of substrate surface is performed with DFT calculations. The adhesion energy of the polymer on substrate is defined as

$$E_{ad,p} = E_{s-p} - E_s - E_p \tag{2}$$

where $E_{ad,p}$ is the adhesion energy of polymer on substrate, E_{s-p} is the energy of system consisting of the substrate and polymer, E_s, E_p are the energy of the substrate and polymer, respectively.

Similarly, the adhesion energy of polymer under the influence of impurities is defined as

$$\Delta E_{ad,p} = E_{s-i-p} - E_{s-i} - E_p \tag{3}$$

where E_{s-i-p} is the energy of system consisting of the substrate, polymer and impurities, E_{s-i} is the energy of the substrate and impurities.

The adsorption energy of impurity on substrate is defined as

$$E_{ad,i} = E_{s-i} - E_s - E_i \tag{4}$$

where E_i is the energy of impurity. The effect of impurity on the polymer adhesion is considered based on two factors. Firstly, the adhesion strength will be weakened if the impurity atoms decrease the adhesion energy. Secondly, if the impurity atoms occupy the same site that the polymer atoms need, the adhesion will be decreased.

3. Results and discussions

3.1. Important crystal faces

Fig. 1 is the morphology of gold obtained by BFDH law. Accordingly, the thinner the thickness of a face, the larger the face will be. And in the end, it will become the major growth face. Table I lists the top three important faces according to their relative thickness. From the data on the second column of Table I, it can be found that the morphology importance of the three faces is in the order of Au(111) > Au(110) > Au(100).

TABLE I The relative thickness of three important faces and their corresponding slice energies from DFT calculations

(hkl)	Relative thickness $d_{(\mathrm{hkl})}/d_{(111)}$	Slice energy (Hatree)
111	1	−1370.8
100	1.16	−1333.5
110	1.64	−1270.3

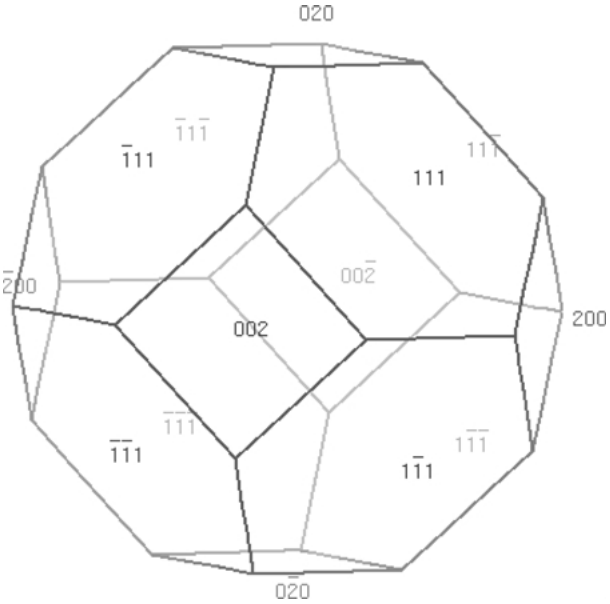

Figure 1 Morphology of crystal gold.

The last column of Table I is the calculated slice energy by Equation 1. It can be seen that the Au(111) face has the lowest energy, therefore, it could be the most stable growing face. In addition, the slab-DFT calculation leads to the same morphology importance order as that obtained by BFDH law.

3.2. The adhesion of the polymer on substrate

The adhesion of polymer on three different gold crystal faces is investigated by geometry optimisation with DFT method. The polymer used in wafer fabrication process is represented by a fragment methyl acetate $C_3H_6O_2$ [11]. The gold substrate, which is fixed during optimisation, is simulated by a periodic geometry with 32 Au atoms (Fig. 2).

Through geometry optimisation, it is found that the polymer bonds to the Au substrate by means of its

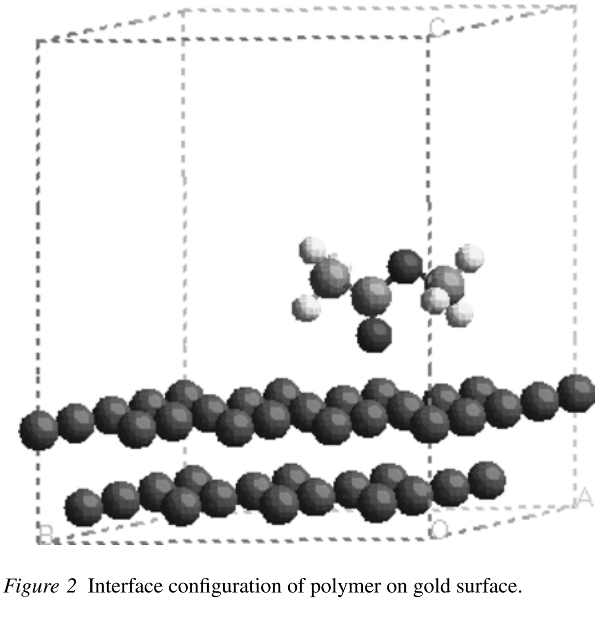

Figure 2 Interface configuration of polymer on gold surface.

TABLE II The corresponding energy for three face E_s, the polymer on top of three face E_{s-p}, and the adhesion energy between polymer and different face $\Delta E_{ad,p}$

Gold face index	E_s (Hatree)	E_{s-p} (Hatree)	$\Delta E_{ad,p}$ (kJ/mol)
(100)	−4339.9072	−4606.2477	−51.72
(110)	−4339.6035	−4605.9427	−48.31
(111)	−4340.0995	−4606.4379	−46.21

Note: the energy of polymer is −266.3208 Hatree.

carbonyl oxygen. The distance between the oxygen of carbonyl and the Au atom is 0.274 or 0.280 nm (with regards to two different sites), which is larger than the sum of covalent radius of Au and O (0.207 nm). Table II lists the calculated energies E_s and E_{s-p}. The adhesion energy, which is derived from Equation 2, is also shown in Table II. From Table II it can be seen that the adhesion energy is in the range of tens kJ/mol, suggesting that the adhesion of the polymer on Au substrate might be difficult in general. In addition, the longer distance (compared to the sum of covalent radius of Au and O) between the oxygen of carbonyl and the Au atom also reflects a weaker adhesion between the polymer and substrate. However, the difference in adhesion energy is still observed among three faces. The relative value of the adhesion energies implies that among the three faces Au(111) may not be in favour of polymer adhesion, although it was identified as the major crystal growth face. On the contrary, Au(100) becomes the preferred face for polymer adhesion. This calculation may suggest that in the etching process of wafer fabrication, a specific etching solvent may be selected that produces the Au(100) surface prior to the polymerisation process.

3.3. Effect of impurities on the adhesion of Au(111) surfaces

To investigate the effect of impurity on adhesion, Au(111) face is selected, and the geometry optimisation of impurity on top of Au(111) surface is carried out. The considered impurities include C, Si, Na, OH and H_2O. After geometry optimisation, the adsorption energies of impurities are calculated according to Equation 4, and shown in the fourth column of Table III. It is found that except water molecule with adsorption energy of −34.1 kJ/mol, the adsorption energy of other impurities is large. This suggests that most of the other impurities can be adsorbed on the Au(111). Since in a real industrial process these impurities may be introduced to the substrate before the polymerisation process, the impurity atoms occupy the sites needed by the polymer. Therefore, these impurities are unfavourable to the adhesion of polymer on the Au.

TABLE III The energy of impurities E_i, totoal energy of impurity on Au(111) E_{s-i}, the adsorption energy $E_{ad,i}$, the total energy of surface, impurity and polymer E_{s-i-p}, and the adhesion energy $\Delta E_{ad,p}$

Impurity	E_i (Hatree)	E_{s-i} (Hatree)	$E_{ad,i}$ (kJ/mol)	E_{s-i-p} (Hatree)	$\Delta E_{ad,p}$ (kJ/mol)
C	−37.4243	−4377.7635	−629.4	−4644.1018	−45.9463
Si	−288.1929	−4628.4671	−458.7	−4894.8049	−44.6335
O	−74.4707	−4414.7724	−530.6	−4681.1106	−45.6837
NaOH	−236.6122	−4576.9299	−573.1	−4843.2575	−17.8534
H_2O	−75.8925	−4416.0049	−34.1	−4682.3395	−36.2319

Table III also lists the adhesion energies (last column) of polymer on the Au(111) substrate under the influence of impurities. This is obtained by further geometry optimisation of substrate with impurity and polymer. Comparing the adhesion energy (46.21 kJ/mol) of polymer on Au(111) without impurity, it can be seen that all impurities reduce the adhesion strength. In addition, the effect of H_2O and NaOH is quite obvious as the adhesion energy decrease to 36.2 and 17.8 kJ/mol, respectively. As mentioned before, the weak adhesion between polymer and gold may due to the formation of weak covalent bonds. The adsorbed impurities may also form the covalent bonds with the Au, which would reduce the electronic density of Au to the bonding to carbonyl oxygen. Therefore, the existence of these impurities will reduce the adhesion, and they should be removed.

4. Conclusion

This study reports a computational simulation of the adhesion between photo-resist polymer and gold substrate. The important crystal growing faces were determined through BFDH law and DFT calculations. The polymer adhesion on three important crystal faces was investigated. The impurity effect on adhesion was also studied by using Au(111) face as an example. Results showed that in general the adhesion between the polymer and Au substrate is weak, regardless of any crystal faces. But the adhesion between polymer and Au(100) face is relatively stronger comparing with another two faces. In addition, the presence of minor impurities could further damage the adhesion. Based on these results, we suggest applying a coupling agent as a medium to improve the adhesion since the polymer/gold adhesion is very poor.

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