Effect of Sputter Deposition on the Adhesion and Failure Behavior between Cu Film and Glassy Calcium Aluminosilicate: A Molecular Dynamics Study

Hyunhang Park and Sunghoon Lee *

Corning Technology Center Korea, Corning Precision Materials Co., Ltd., 212 Tangeong-ro, Asan 31454, Chungcheongnam-do, Korea; hyunhangpark@corning.com
* Correspondence: sunghoonlee@corning.com

Abstract: Understanding the physical vapor deposition (PVD) process of metallic coatings on an inorganic substrate is essential for the packaging and semiconductor industry. In this work, we investigate a Copper (Cu) film deposition on a glassy Calcium Aluminosilicate (CAS) by PVD and its dependence on the incident energy. Molecular dynamics simulation is adopted to mimic the deposition process, and pure Cu film is grown on top of CAS surface forming intermixing region (IR) of Cu oxide. In the initial stage of deposition, incident Cu atoms are diffused into CAS bulk and aggregated at the surface which leads to the formation of IR. When the high incident energy, 2 eV, is applied, 20% more Cu atoms are observed at the interface compared to the low incident energy, 0.2 eV, due to enhanced lateral diffusion. As the Cu film grows, the amorphous thin Cu layer of 1 nm is temporarily formed on top of CAS, and crystallization with face-centered cubic from amorphous structure follows regardless of incident energy, and surface roughness is observed to be low for high incident energy cases. Deformation and failure behavior of Cu-CAS bilayer by pulling is investigated by steered molecular dynamics technique. The adhesive failure mode is observed, which implies the bilayer experiences a failure at the interface, and a 7% higher adhesion force is predicted for the high incident energy case. To find an origin of adhesion enhancement, the distribution of Cu atoms on the fractured CAS surface is analyzed, and it turns out that 6.3% more Cu atoms remain on the surface, which can be regarded as a source for the high adhesion force. Our findings hopefully give the insight to understand deposition and failure mechanisms between heterogeneous materials and are also helping to further improve Cu adhesion in sputter experiments.

Keywords: Cu film; aluminosilicate glass; sputter; molecular dynamics; metal-inorganic interface; pulling force; adhesive failure

1. Introduction

Cu metallization on non-conducting materials such as glasses or ceramic substrates has been one of the great interests in microelectromechanical systems (MEMS), packaging for semiconductors, and display industries [1–4]. The adhesion between Cu film and the oxide glasses (e.g., silicate) is too weak to satisfy the criteria for commercial use of the product [5–7]. Note, Cu and glasses are inherently different kinds of materials from each other in terms of molecular interactions, in other words, the bonding natures of Cu and glasses are metallic and ionic, respectively. According to molecular orbital theory, unlike some late transition metal elements such as Ti or Zr, the outermost electron shell of the Cu element is not fully occupied [8]. Therefore, even if Cu makes bonding with electronegative elements in the glasses such as O, overlaps of electron clouds between them are not dense, which leads to a low bond dissociation energy between Cu and O [9].

To overcome this low adhesion strength due to the intrinsic property of Cu, there have been many persistent engineering efforts to improve the adhesion strength of Cu film on the glasses via various deposition techniques such as electroless plating, chemical
vapor deposition, and sputtering [5,9–12]. Among them, the sputter deposition technique has many advantages in obtaining uniform coating and good adhesion with the metal substrates as well as simplicity in the process development. However, practical adhesion of sputter-deposited Cu film on the glass substrate measured by experiments includes some inaccuracies depending on the kinds of adhesion measurement techniques such as pulling, peeling, or bending tests [5,13–16]. In addition, surface interactions during sputtering and underlying mechanisms for the adhesion and failure phenomena of the deposited film are still lacking.

Molecular dynamics (MD) simulation can be considered as a proper tool for the study of the effect of sputter on the adhesion between Cu film and glass. Firstly, MD simulation can track real-time movements and collisions of all atoms during the process, thereby help to understand the surface interactions between energetic incident atoms and the substrate. Indeed, deposition simulations for many kinds of inorganic films such as C, Ni/Cu/Ni, Al$_2$O$_3$, ZnO, or MgAl$_2$O$_4$ have been studied to reveal the mechanism of bond formation, atomic intermixing at the interface, and stress development [17–21]. Secondly, by mimicking experimental adhesion tests, one can directly calculate quantitative adhesion strength considering all kinds of molecular interactions between Cu film and glass substrate and analyze the failure behavior of the Cu-glass bilayer in nanoscale. This unique method which is called steered molecular dynamics (SMD) makes it possible to monitor the temporal evolution of free energy and applied force of the bilayer system while normal or shear stress is applied. Calculation of energy difference between separate state and adhered state of two layers, the conventional approach, does not guarantee a precise adhesion strength since it cannot consider a conformational change of the materials during the pulling path, especially in case of the interface where different kinds of materials form some mixture. On the other hand, the SMD method is expected to well describe adhesion between heterogeneous materials, as proved in the field of protein folding and deformation behavior of organic-inorganic interfaces [22,23].

In this work, a metal-inorganic bilayer formed by the Cu sputter deposition process on the glassy calcium aluminosilicate (CAS) is investigated by means of molecular dynamics simulations. CAS substrate is initially prepared, then Cu atoms are deposited on the substrate surface to form Cu-CAS bilayer, in which there are two distinct regions as an intermixing region (IR) around the top of CAS and the metallic Cu film on CAS up to 7 nm thickness. Structural features of both IR and Cu film regions are analyzed in detail. To estimate the effect of incident energy of Cu atoms on the adhesion, we compare levels of adhesion forces between high, 2 eV, and low, 0.2 eV, incident energy ($E_{\text{inc}}$) cases. Cu-CAS bilayer is pulled in the z direction by the SMD technique until it is completely separated into two parts. During the pulling test, the temporal evolution of the pulling force is tracked, and adhesion force is calculated along with the failure mode analysis. From this work, the critical factor for the adhesion is suggested, and the relevant mechanism is introduced.

2. Computational Methods

2.1. Materials and Building of CAS Substrate

Metallic Cu and oxide glass are considered as two ingredient materials that make an interface. CAS which belong to silicate glasses containing Al and Ca elements are used as a substrate. It is known that they are widely applied in commercial display glasses as well as electronic devices because of reinforced strength with good machinability [24,25]. The composition of CAS used in this simulation is 5CaO-20Al$_2$O$_3$-75SiO$_2$ in wt %, following the fact that Al composition is much higher than Ca composition in typical display glass. A thin Cu film is formed onto the glass substrate by a deposition process. Since every single Cu atom will be directly deposited in the simulation, any information such as preferred orientations of the Cu film does not need to be assumed. For the construction of CAS substrate, nano-sized glass blocks for the surface composition of CAS are constructed according to a consistent protocol of the melt-quench method. Initially, about 20,000 atoms are randomly located in a rectangular simulation box where periodic boundary conditions
are applied for x, y, and z directions. The size of the box is $6.2 \times 6.2 \times 6.2 \text{ nm}^3$. Then the box is heated from 300 K to 3600 K for 100 ps, melted at 3600 K for 200 ps, quenched with a cooling rate of 5 K/ps for 660 ps, and finally relaxed at room temperature for 200 ps [26–28]. NPT dynamics were used for the heating procedure while melting and quenching procedures were performed with NVT dynamics. Another NPT dynamics simulation was then performed for the gradual release of residual stress in the system. The density of relaxed bulk CAS was 2.54 g/cm$^3$, which is similar to the experimental density of 2.4 g/cm$^3$ within 10% error [29]. Then, the open boundary condition was applied in z direction to create the surface. The lower surface of 0.5 nm thick is fixed in its initial position to play a role of bulk inside while the upper surface is open as an empty space where a set of Cu atoms will be introduced afterward.

2.2. Simulation of the Film Growth by PVD

Figure 1 shows the overall modeling procedure for the deposition of Cu atoms and the pulling process. The deposition simulation is performed in the manner that Cu atoms are continuously dropped downward one by one onto the CAS substrate. Initially, the substrate is located at the bottom of the simulation box. When the simulation begins, a single Cu atom is placed at 5 nm above the substrate surface with the random position in x and y dimensions. The introduced atom is ‘shoot’ pointing downward normal to the substrate with a given velocity. Then it collides with the substrate and forms bonding with atoms of the substrate surface. This protocol is repeated until Cu atoms and substrate atoms interact with each other to generate an interlayer, and roughly 18,000 Cu atoms are deposited to form a 7 nm thickness of film from the top of CAS substrate during 100 ns. Basically, the NVE ensemble is applied to the whole system for energy conservation during collisions between the incident atoms and substrate. However, that protocol also leads to divergence of system temperature due to the continuous supply of incident atoms with high kinetic energies into the system. Thus, an NVT ensemble with 300 K of system temperature is applied to a set of atoms in the lower part of the substrate with 2.5 nm thickness, which means it plays the role of the heat bath. Additionally, the incidence of an atom is controlled to occur every 5 ps. It is known that this time period gives enough ‘cooling’ time so that the thermal fluctuation of the surface is diminished out through the substrate [20,30].

Figure 1. Scheme of modeling procedure for Cu sputter on glassy CAS and pulling process.
Since the current simulation focuses on the surface interaction between incident atoms and substrate, any other effects of process variables such as Ar pressure or Cathode power at the sputtering target are not considered. Two kinds of incident energies 2 eV and 0.2 eV are tested, which shall be referred to as high and low $E_{\text{inc}}$ cases, respectively, throughout the simulation. Value of 2 eV has been used as a typical $E_{\text{inc}}$ level of the sputtered particles in the simulations for metal sputter [18,30,31], whereas 0.2 eV is low enough to even represent the energy level of the heated particles in the evaporation process. For a clear comparison of the effect of $E_{\text{inc}}$ difference, the flux for both cases was fixed to be the same. The incident angle was set to be normal to the substrate throughout the simulation.

The whole simulation procedures described in Figure 1 were performed using the LAMMPS simulation package [32]. To describe both ionic and metallic interactions, two kinds of interatomic forcefields were used. The one is a non-bonded type Morse potential developed by Pedone et al. which has been proved to be good for a description of silicate glass [26–28], and the other is an embedded atom method (EAM) potential for Cu element optimized for the study of metal properties [33]. EAM potential parameters between different cations such as Cu, Al, Ca, and Si was not considered in this simulation since mainly required interactions relevant to adhesion and failure behavior are ionic interaction in IR and metallic interaction between Cu only in Cu film side. Both potentials were applied simultaneously during the whole deposition process. It is noted that electric neutral charges were applied to incident Cu particles during metal film growth since EAM potential does not require a fixed value for charge whereas Cu in IR was remained positively charged. We believe this is the most reasonable way to apply a fixed-charge potential to heterogeneous metal-inorganic bilayer since the Cu atom has a neutral charge when ejected from a sputtering target, but will be immediately polarized through hybridization between O 2p and Cu 3d electron state as soon as it makes a close contact to oxide network within its ionic radius [34]. The time step and cutoff for van der Waals interactions for simulation were set to be 1 fs and 12 Å, respectively. The Particle-Particle Particle-Mesh (PPPM) solver is used for the summation of long-range Coulomb interactions with the precision of $10^{-4}$.

2.3. SMD Simulation and Adhesion Calculation

To calculate adhesion force and monitor the failure behavior at the interface between sputter-deposited Cu and CAS substrate, we applied the SMD technique to mimic the experimental pulling test. SMD technique has been utilized to estimate the interfacial adhesion and analyze conformational changes of the polymer systems [22,35–38] and bio-materials [23,39]. In this technique, a fictitious atom is connected to the center of mass (COM) of the system of interest by a virtual spring with a spring constant $k$ at the outside the system, and the atom pulls it along the normal direction to the CAS substrate with a constant velocity $v$. During the pulling process, the total force and the potential energy are calculated as following equations:

$$U_{\text{spring}} = \frac{1}{2}k[vt - (R(t) - R_0) \cdot \mathbf{n}]^2$$  \hspace{1cm} (1)

$$F_{\text{spring}} = -\nabla U_{\text{spring}}$$  \hspace{1cm} (2)

where $R(t)$ is the current position of the COM of the system, $R_0$ is the initial center of mass of the system, and $n$ is a unit vector along the direction in which the spring is pulled. Then the total work done is calculated as:

$$W = \int_{r=R_0}^{r=R_f} \nabla U_{\text{spring}} \cdot d\mathbf{r}$$  \hspace{1cm} (3)
where $R_f$ is the final position of the COM of the system. It is well known that the ensemble average of total work done can be regarded as the potential of mean force (PMF) using Jarzynski equality \cite{40, 41}:

$$\langle \exp(-\beta W) \rangle_{\text{ensemble}} = \exp(-\beta U_{\text{PMF}})$$

(4)

where $\beta = \frac{1}{k_B T}$, $k_B$ is the Boltzmann constant and $T$ is the temperature. Cu film and the CAS substrate are pulled apart along positive and negative $z$ direction respectively, with a constant velocity of 10 m/s. The value of the pulling velocity was determined in such a way that adhesion value approached a saturation point for velocity values lower than 10 m/s.

3. Results and Discussion

3.1. Formation of Intermixing Region (IR)

Figure 2 briefly shows snapshots of the local surface structure of CAS substrate during the incidence of Cu atoms onto it. It is well known that the surface of silicate glass including alkali or alkali-earth elements has high-membered ring structures and defective sites such as tri-clustered oxygen and under-coordinated Si or Al \cite{42}. Figure 2a shows a local network structure that is comprised of two 4-membered rings and one 7-membered ring. The ring structures are denoted by a grey dotted line, and only Si-O and Al-O bonds are visualized because Si and Al are network formers of CAS glass. Two 4-membered rings share one corner with one tri-clustered oxygen. Figure 2b exhibits a first incident Cu atom which is adsorbed in the middle of a 7-membered ring. It is notable that its collision with high kinetic $E_{\text{inc}}$ of 2 eV did not result in the breakage of the silica network itself which means the ring structure is energetically stable. Interestingly, as shown in Figure 2c, we observe that when another incident Cu atom attacks a corner that 4-membered and 7-membered ring shares as denoted in the green line, the Al-O bond is broken and a 9-membered ring is formed. It implies same $E_{\text{inc}}$ may induce a change of ring structure when the collision occurs around the weak side. Figure 2c also shows that newly incident Cu atom aggregates to first incident Cu due to their metallic character within the 9-membered ring. Since the newly formed 9-membered ring is energetically not stable due to the 3-coordinated Si atom in its right corner, an aggregated Cu pair diffuses into the CAS to find its local energy minima, and the 4- & 7-membered ring structures are restored as shown in Figure 2d. In this way, the incident Cu atoms continuously transfer additional energy to the surface, where they can penetrate deeper into the CAS bulk region or form aggregates or clusters to cover the surface which leads to the formation of IR. In addition, thermal heating is also observed due to the collision of atoms, and temperature increases up to 500 K during 30 ns.

![Figure 2](image-url)

**Figure 2.** Incidence of Cu atoms to the local network on CAS surface: (a) Local silica structure with two 4-membered rings and one 7-membered ring (grey dotted line), and one tri-clustered oxygen (b) Incident Cu is adsorbed into the 7-membered ring (dark shaded region) (c) One of the bonds in the 4-membered ring is broken (green oval) due to incidence of another Cu atom (d) Aggregated Cu pair rotates to find its relaxed location in the 7-membered ring, then Al-O bond is recreated (cyan oval) and the 4-membered ring is restored.
Figure 3 presents two snapshots and cross-sections of the CAS substrate depending on $E_{\text{inc}}$ at the same time frame during the stage of IR formation. This stage may be roughly referred to as when Cu film almost fully covers the CAS surface. We observe that some Cu atoms weakly adsorbed on the surface form island-type aggregates. Since it is hard to find a difference in surface coverages of Cu between high and low $E_{\text{inc}}$ cases, the position of incident Cu along $z$ direction is analyzed. Figure 4 shows the distribution of Cu atoms near the CAS surface at the time frame of snapshots in Figure 3. To analyze the effects of high and low $E_{\text{inc}}$ cases on the distribution of Cu, we divide $z$ coordinate into three distinct regions of 48–55 Å, 55–61 Å, and 61–66 Å which will be referred to as region I, II, and III, respectively. It is observed that the black line is located over the red line in region I and III, which indicates that more Cu atoms exist in both regions when we apply high $E_{\text{inc}}$. In region III, it is expected that they form denser ionic bonds with silicate networks, and in region I, more Cu atoms deeply diffuse into CAS bulk as described in the inset. Since the total number of incident Cu atoms are the same for both cases, in region II, one can conjecture more Cu atoms are located for the low $E_{\text{inc}}$ case (red line in the figure) than the high $E_{\text{inc}}$ case. It is not surprising that the distribution of Cu shows a difference depending on the regions because incident Cu atoms for high $E_{\text{inc}}$ case will be more actively moved to both the lateral direction and vertical direction. Table 1 quantitatively compares the number of Cu atoms depending on the regions between high and low $E_{\text{inc}}$ cases. In regions I and III, we find that the high $E_{\text{inc}}$ case exhibits 48 and 20% more Cu atoms than the low $E_{\text{inc}}$ case, respectively. We can summarize the results as follows: In the high $E_{\text{inc}}$ case, due to the high kinetic energy of incident Cu atoms, they actively diffuse to both lateral and vertical directions, and thus they are strongly aggregated near the surface and penetrate more deeply into the CAS bulk. On the other hand, in the low $E_{\text{inc}}$ case, much of Cu atoms are relaxed around their initial incident positions and are diffused into the bulk region before they meet to be aggregated.

Table 1. Comparison of a number of Cu atoms in IR between high and low $E_{\text{inc}}$ cases for three regions along the $z$-direction. Numbers in red font mean that there are more Cu for that $E_{\text{inc}}$ case.

| Regions in $z$ Coordinate | Number of Cu for High $E_{\text{inc}}$ Case | Number of Cu for Low $E_{\text{inc}}$ Case |
|---------------------------|------------------------------------------|------------------------------------------|
| Whole region (48–66 Å)    | 769                                      | 769                                      |
| Region I (48–55 Å)        | 34                                       | 23                                       |
| Region II (55–61 Å)       | 503                                      | 552                                      |
| Region III (61–66 Å)      | 232                                      | 194                                      |

**Figure 3.** Comparison of IR on CAS substrate between (a) high $E_{\text{inc}}$ and (b) low $E_{\text{inc}}$ cases. Atom sizes of glass elements were reduced in the top view for emphasizing the adsorption of Cu atoms.
Figure 3. Comparison of IR on CAS substrate between (a) high E\textsubscript{inc} and (b) low E\textsubscript{inc} cases. Atom sizes of glass elements were reduced in the top view for emphasizing the adsorption of Cu atoms.

Figure 4. Comparison of $z$ position of Cu distribution in CAS between high and low E\textsubscript{inc} cases during the stage of IR formation. Region I and III show that there are more Cu for the high E\textsubscript{inc} case, whereas region II shows that there are more Cu for the low E\textsubscript{inc} case. The difference in Cu numbers between high and low E\textsubscript{inc} cases is magnified in the inset.

Table 1. Comparison of a number of Cu atoms in IR between high and low E\textsubscript{inc} cases for three regions along the $z$-direction. Numbers in red font mean that there are more Cu for that E\textsubscript{inc} case.

| Regions in $z$ Coordinate | Number of Cu for High E\textsubscript{inc} Case | Number of Cu for Low E\textsubscript{inc} Case |
|---------------------------|-----------------------------------------------|-----------------------------------------------|
| Whole region (48–66 Å)   | 769                                          | 769                                          |
| Region I (48–55 Å)       | 34                                           | 23                                           |
| Region II (55–61 Å)      | 503                                          | 552                                          |
| Region III (61–66 Å)     | 232                                          | 194                                          |

3.2. Cu Film Growth on IR

After the stage of IR formation, Cu atoms are continuously deposited to form Cu film. As described in the previous subsection, some Cu atoms gather together by diffusion on the surface to form island-type aggregates. It becomes a seed for nucleation of Cu film, and growth of Cu film is initiated following Volmer–Weber mode of thin metal film growth [43]. Figure 5a describes crystallization of Cu film structure with their thickness change from 1 nm to 7 nm by common neighbor analysis (CNA) during deposition process [44]. We observe the film initially takes an amorphous structure following the shape of CAS surface during 1 nm growth. This amorphization can be attributed to huge lattice strains and distortion applied to a bottom thin layer of Cu film due to direct bonding with amorphous CAS [45]. It is also consistent with the fact that an amorphous layer appears for both E\textsubscript{inc} cases, which suggests that potential energy by lattice strain is much higher than the level of the incident kinetic energy of Cu atoms. On the other hand, crystallinity shows up as the Cu film grows more than 1 nm thickness. This crystalline structure is maintained until the whole deposition process is finished, and CNA indicates the crystalline structure of Cu mainly belongs to the fcc crystal structure. X-ray diffraction analysis is also performed to check the crystallographic information of the film as shown in Figure 5b. When Cu film is 1 nm thick, the intensity is very broadly dissipated over the range of 2 theta degree which implies the overall structure is still amorphous. However, after deposition ends, new peaks are developed at the values of 43.4°, 50.2°, and 73.7° whose corresponding surface orientations are (111), (200), and (220) of fcc, respectively. Since the main peak among them is (111), one can say that the Cu film grown in this simulation is a single crystal, and its preferred orientation along the z-axis is (111) [46].
Figure 5. (a) Crystallization of Cu film during deposition process (substrate part was not shown for clear comparison). In the 1 nm thickness, the film shows an amorphous structure (left), but the film is crystallized when it grows as 7 nm thickness (right) (b) X-ray diffraction (XRD) patterns of Cu film grown in the simulation.

Figure 6 shows typical surface morphologies of Cu film after deposition for high and low $E_{\text{inc}}$ cases. Comparison between Figure 6a,b gives a striking difference in surface morphologies of Cu film between high and low $E_{\text{inc}}$ cases. One readily finds that the surface of Cu film for the high $E_{\text{inc}}$ case is almost flat. On the other hand, the low $E_{\text{inc}}$ case yields much of the peaks and valleys with some pores inside the film, which results in high surface roughness. This difference is not surprising because incident particles with high $E_{\text{inc}}$ not only help rearrangement of surface silica networks by the collision but also themselves actively hop over the surface to create a flat terraced structure. This mechanism is called atomic peening [47]. Meanwhile, if incident particles have low energies then it is not easy for them to arrive at valley points, and thus peak points have more chances to be deposited than valley points which are referred to as the shadowing effect [48].

Figure 6. Surface morphology of Cu films grown onto CAS substrate: (a) high $E_{\text{inc}}$ and (b) low $E_{\text{inc}}$ case.
### 3.3. Deformation and Failure of Cu-CAS Bilayer

In this subsection, pulling simulation is performed to Cu-CAS bilayer along $z$ direction. As mentioned in Section 2.3, a set of Cu atoms in a rectangular region whose thickness is half of the Cu film are pulled upward by a virtual spring. As pulling simulation begins, tensile stress is applied to the bilayer and induces severe strain of the bilayer along $z$ direction. This strain is represented by the increased center of mass (COM) of pulled Cu atoms, which is called pulling distance. One can monitor the continuous change of force during pulling until the bilayer experience a failure. Figure 7a shows typical temporal curves of pulling force as a function of pulling distance. As pulling distance increases, the pulling force also increases which implies that the bilayer withstands its molecular interactions against the external harmonic force. However, it draws a maximum at around 9 Å of pulling distance, then rapidly diminishes to zero. This abrupt change corresponds to a failure of bilayer at that distance, and the maximum value of pulling force can be regarded as an adhesion force. It is notable that the difference in the shape of the force curve between high and low $E_{\text{inc}}$ cases gives a clue for structural features of the Cu-CAS interface. Around the point of maximum pulling force, it seems that the high $E_{\text{inc}}$ case undergoes more severe strain hardening, while the low $E_{\text{inc}}$ case shows more ductile behavior which is inferred from the low slope. Figure 7b compares maximum pulling forces between high and low $E_{\text{inc}}$ cases, averaged over 5 samples for each. The calculation result exhibits that the high $E_{\text{inc}}$ case shows a 7% of higher adhesion force than the low $E_{\text{inc}}$ case.

![Figure 7. Comparison of adhesion force between high and low $E_{\text{inc}}$ cases: (a) evolution of pulling force as a function of pulling distance (b) level of maximum pulling force.](image)

To clearly analyze how $E_{\text{inc}}$ affects adhesion force, we firstly focus on the region of failure and morphology of the fractured surface. One can imagine three possible locations of failure, which are inside the CAS, the interface between CAS and amorphous Cu layer, and inside Cu film. Among them, we observe the bilayer experiences a failure at the interface between CAS and amorphous Cu layer for both high and low $E_{\text{inc}}$ cases as shown in Figure 8. In other words, it undergoes an adhesive failure irrespective of the incident energy and implies the interface is the weakest part of the bilayer system. This is not surprising because the other two locations are essentially bulk regions of glass and Cu film, and their cohesive strengths are expected to be high compare to the interface. Furthermore, the top view in Figure 8 indicates that Cu is a main element on the fractured surface. As mentioned in the previous subsection, Cu atoms act as a nucleation site at the interface, and thus the number of Cu atoms on the CAS surface would be a major contributor to the adhesion strength.
For quantitative analysis, the number of atoms, specifically, Cu and O are counted along the z direction and presented in Figure 9. As already indicated in Figure 4 and Table 1, there were 20% more Cu atoms on the CAS surface for the high E\textsubscript{inc} case compared to that for the low E\textsubscript{inc} case during the stage of IR formation. A similar trend is observed on the fractured surface when comparing Figure 9a,b. The green area in the graph represents additional Cu atoms at the surface after the formation of Cu oxide assuming that amount of interstitial Cu in the oxide is negligible, and thus it can be regarded as exposed Cu atoms on the fractured surface. As shown in Figure 9c, there are 6.3% more Cu atoms in the green area for the high E\textsubscript{inc} case than that for the low E\textsubscript{inc} case. These additional Cu atoms mainly form metallic bonding with Cu film, and thus finally lead to 7% higher adhesion for the high E\textsubscript{inc} case. Based on the analysis so far, we can propose a mechanism of the whole procedure of Cu deposition, and clarify the origin of the difference in adhesion.

In the stage of IR formation, due to active lateral and vertical diffusion, around 20% more Cu atoms with high E\textsubscript{inc} were distributed to the surface than those with low E\textsubscript{inc}. Although some of the Cu atoms may diffuse into Cu film and glass during the whole deposition process, the growth of thick Cu film onto it effectively conserves the shape and composition of IR, and thus some more Cu atoms could still remain at the Cu-CAS interface as an amorphous thin layer. These excessive Cu atoms finally resulted in higher adhesion than the low E\textsubscript{inc} case. Even though the difference in adhesion value between high and low E\textsubscript{inc} cases looks to be small, we emphasize that our results showed control of a single sputter process parameter can bring into an increase of adhesion with an understanding of the underlying mechanism by analysis of its failure behavior. Based on this understanding, it is expected that changes of other parameters such as raise of incident ion flux can, even more, increase the adhesion in the experiment. Also, if one aims to further increase adhesion, we can attempt to control the bonding strength of an amorphous thin layer of Cu which is another factor for adhesion force irrespective of E\textsubscript{inc}. For example, an increase in the amount of oxygen at the CAS surface by surface treatment with oxygen plasma will lead to enhancement of bonding strength of the amorphous Cu layer.

**Figure 8.** Adhesive failure of Cu-CAS bilayer and top view of the surface after the failure for (a) high E\textsubscript{inc} and (b) low E\textsubscript{inc} cases.
Figure 9. Count of O and Cu atoms along z coordinate around the fractured CAS surface for (a) high E\text{inc} case and (b) low E\text{inc} case. Shaded regions represent the number of Cu atoms that are expected to form metallic bonds with Cu film, thus contributing to adhesion strength. (c) Comparison of a number of Cu atoms in the green regions for high and low E\text{inc} cases.

4. Conclusions

To find the effect of incident energy of sputter deposition, adhesion and failure behavior of Cu-CAS bilayer is investigated by molecular dynamics simulations. High and low E\text{inc} of 2 eV and 0.2 eV, respectively, are compared throughout the deposition process and pulling test. In the stage of IR formation, it is observed that incident Cu atoms are diffused into bulk CAS and are aggregated near the surface. It turns out that 20% more Cu atoms for the high E\text{inc} case are distributed at the surface than that for the low E\text{inc} case due to active lateral diffusion with their high kinetic energies. During the stage of Cu film growth, incident Cu atoms are nucleated to form a metallic Cu film with crystallization of fcc type. Irrelevant to incident energy, an amorphous thin layer of Cu is initially grown as 1 nm thickness due to high lattice strains by the bonding with CAS while crystallization of Cu film is observed when the film is deposited more than 1 nm height. High and low E\text{inc} cases disclose a clear difference in their surface morphologies, namely, low and high surface roughness of the film, respectively. Pulling test with SMD technique reveals that failure occurs at the interface between Cu film and CAS for both high and low E\text{inc} cases, while the former gives 7% higher adhesion force than the latter. Analysis for z positions of O and Cu atoms at the fractured CAS surface shows that there are 6.3% more Cu atoms at the surface for the high E\text{inc} case compared to the low E\text{inc} case. It is suggested that additional Cu atoms remained after participating in the formation of Cu oxide from metallic bonding with Cu film, which finally leads to higher adhesion. Our work ultimately implies that an effect of even a single process variable such as incident energy can result in the non-negligible difference in surface structure and failure behavior. We believe our finding will be helpful to understand the deposition mechanism as well as structure-property relations for the interface between heterogeneous materials.

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