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Citation	Surface and Coatings Technology (2011), 206(5): 845-848
Issue Date	2011-11
URL	http://hdl.handle.net/2433/151702
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Type	Journal Article
Textversion	author

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Chemical erosion and sputtering of solid surfaces with liquid cluster ions

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Abstract

The sputtering phenomena of solid surfaces such as Si(111) and SiO_2 surfaces were investigated using ethanol and water cluster ion beams. To be compared with Ar monomer ion irradiation, the sputtering yield of Si surfaces was approximately 100 times higher for ethanol cluster ion irradiation and approximately 10 times higher for water cluster ion irradiation. Furthermore, for the ethanol cluster ion irradiation, chemical erosion such as silicon hydride and hydro-carbide reaction occurred on the Si surface, which resulted in the high-rate sputtering of the surface. On the other hand, for the water cluster ion irradiation, oxidation occurred on the Si surface, and physical sputtering was performed on the surface. Based on these results, chemical reaction at a nano-scale area on the Si(111) surfaces was discussed from the thermodynamic approach, and the impact of cluster ions on the surface exhibited high temperature such as a few tens of thousands degrees, which resulted in the enhancement of the chemical reaction. Thus, liquid cluster ion irradiation exhibited unique erosion and sputtering even at room temperature, which were not obtained by a conventional wet process.

Keywords: Liquid cluster, Ion beam, Chemical erosion, Sputtering, Silicon

1. Introduction

Sputtering is fundamental phenomenon caused by the bombardment of energetic particles on a solid surface. It has received much attention from experimental and theoretical viewpoints [1-3]. In addition, sputtering is used for many applications and has become an indispensable process in modern technology and physics [4, 5]. One of the applications is the deposition of thin films on various kinds of substrates. Another application is various kinds of surface treatments such as etching, cleaning and polishing. If sputtering allows a controlled removal of surface layers on a nearly atomic scale, it can be applied to the formation of very clean surfaces as well as very smooth surfaces. For these applications, high rate sputtering and smooth surface formation are key issues.

The cluster ion beam process has attracted much interest from both fundamental and applied viewpoints [6, 7]. As well as the properties of the cluster itself, the impact process of an energetic cluster ion on a solid surface represents specific features. Compared with the monomer ion beam process, the cluster ion beam technique has several advantages, one of which is that high-energy-density deposition and the collective motions of the cluster atoms play important roles in the surface process kinetics. Another advantage is that equivalently low-energy and high-current ion beams can be realized using cluster ion beams. Furthermore, liquid cluster ion beams represent unique properties in sputtering [8, 9]. High rate sputtering and smooth surface formation have been achieved even at room temperature by adjusting the kinetic energy of the liquid cluster ions. In this article, sputtering phenomena of Si(111) and SiO_2 surfaces by ethanol and water cluster ion beams are investigated. Furthermore, physical and chemical sputtering by the ethanol cluster ion beams is discussed from experimental and theoretical viewpoints.

2. Experiment

The liquid cluster ion beam system was described elsewhere [10]. Briefly, liquid materials such as ethanol and water were introduced into a cluster source through a valve. The liquid materials were heated up to 150℃ by a wire heater attached around the source.

The vapors were ejected through a nozzle into a vacuum region. When the vapor pressure was larger than 1 atm, ethanol and water clusters were produced by an adiabatic expansion. The liquid clusters produced passed through a collimator and entered an ionizer. In the ionizer, the neutral clusters were ionized by an electron bombardment method. The cluster ions were accelerated by applying an extraction voltage to the extraction electrode. The cluster ions extracted were size-separated by a retarding potential method, and the minimum size of the cluster ions was adjusted by the retarding voltage. The cluster ions with a size larger than the minimum size were accelerated toward a substrate, which was set on a substrate holder. In this system, the minimum size of the cluster ions was 100 molecules per cluster, and the acceleration voltage was adjusted between 0 kV and 10 kV. The ion dose to the substrates was determined based on the ion current measured. When the desired ion dose was attained, the shutter was closed to terminate ion irradiation. The substrates used were Si(111) and SiO_2, and the substrate temperature was room temperature.

The cluster size distribution was measured by a time-of-flight (TOF) method. The principle of this method is based on the fact that the time of flight is proportional to a square root of mass. The accelerated cluster ions entered a flight tube, and were deflected by a pulsed negative-voltage. When the pulsed voltage was applied, the cluster ions drifted toward a Faraday cup mounted on the end of the flight tube. The cluster size was measured based on the drift time ranging from μsec to msec, which was different depending on the mass. The cluster size was distributed between a few hundreds and a few tens of thousands, and the average size (peak size) was approximately 1500 molecules per cluster for the ethanol cluster and approximately 2500 molecules per cluster for the water cluster, respectively.

3. Experimental results

Fig. 1 shows the dependence of sputtered depth for Si(111) and SiO_2 surfaces on acceleration voltage for ethanol and water cluster ions. The ion dose was 1.0 x 10^{16} ions/cm^2,

and the cluster size used was larger than 100 molecules per cluster. As shown in the figure, the sputtered depth increases with increase of the acceleration voltage. When the acceleration voltage is 9 kV, the sputtered depth by the ethanol cluster ion irradiation is 356 nm for Si and 47 nm for SiO_2, respectively. The sputtering ratio of Si to SiO_2 is approximately 8. Taking account of the sputtered depth and the ion dose, the sputtering yield can be calculated by estimating the density of Si and SiO_2 such as 2.42 g/cm^3 and 2.63 g/cm^3, respectively. The sputtering yield of Si is 185 atoms per ion, which is approximately 100 times larger than that by argon (Ar) ion beam sputtering. After bombardment of the ethanol cluster ions, hydrogen atoms and alkyl radicals are produced, and they react with the Si surface atoms [6]. The selectivity arises from the volatility of the reaction products and the difference in binding energy among the materials. This suggests that chemical reactions between Si atoms and ethanol molecules produce silicon hydride and silicon hydro-carbide which are the dominant etching materials for the Si surfaces.

On the other hand, for the case of water cluster ion irradiation, the sputtered depths of Si and SiO_2 are almost the same. This is ascribed to the physical sputtering by the water cluster ion irradiation. After bombardment of the water cluster ions on the Si surfaces, the surface oxidation occurs. The erosion process such as oxidation depends on both the kinetic energy and the reactivity of the bombarding species. The OH radicals and oxygen atoms produced after the bombardment have important roles in the oxidation due to the implantation and/or diffusion processes. Since the silicon oxide layer has a higher surface binding energy than the Si surface, chemical effects in the sputtering of the oxide layer decrease. Instead, the kinetic energy of another cluster ion bombarded is transferred to the physical sputtering of the oxide layer. As a result, the sputtered depth of Si surfaces is similar to that of SiO_2 surfaces.

The surface state of the Si substrates irradiated by the ethanol cluster ion beams was investigated by X-ray photoelectron spectroscopy (XPS) measurement. Fig. 2 shows the depth profile of (a) O1s and (b) C1s peaks for the Si surface irradiated at an acceleration voltage of 9 kV. Compared with the peak at the surface without etching, the peaks for etched

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surfaces appear at lower energies. This is ascribed to the presence of the ethanol molecule or its fragment such as CO radical. After etching the surface by 0.75 nm, both O1s and C1s peaks become very weak. This indicates that ethanol molecule or its fragment is present near the Si surface irradiated, and they are implanted into the Si surface within a depth less than 1 nm.

With regard to the water cluster ion irradiation, the XPS measurement showed that Si2p peak for the Si surface irradiated was shifted to the higher value of binding energy, which corresponded to the peak for SiO_2. However, the Si2p peak for SiO_2 decreased with increase of the depth, and it disappeared at a depth of 10.7 nm for the water cluster ion irradiation at an acceleration voltage of 9 kV. This indicated that the silicon oxide layer was formed by the water cluster ion irradiation, and the oxide layer thickness was approximately 10 nm.

The sputtered particles from the Si(111) surface were collected on an Au substrate, and they were investigated by the XPS measurement. Fig. 3 shows the Si2p peaks for the particles released at an ejection angle of (a) 10° and (b) 80°. The ejection angle of 0° is defined to be normal direction. The Si2p peaks corresponding to SiH_x and $Si(CH_3)_4$ appear at 99.4 eV and 100.2 eV, respectively. Another peak appeared at 102.2 eV corresponds to a Si-O bonding. After impact of the ethanol cluster ion on the Si surface, hydrogen atoms as well as various kinds of radicals such as CH_3 and OH are produced, and the chemical reaction of these radicals with the Si surface atoms occurs. For example, hydride and oxide reactions as well as organic reaction occur, which result in producing SiH_x and SiO_x as well as $Si(CH_3)_4$. With regard to the SiO_x product, it is removed from the surface by the irradiation of another cluster ion. In the physical sputtering, such as the removal of SiO_x product, the lateral sputtering effect by the cluster ion irradiation is enhanced, and the SiO_x particles are ejected along the Si surface. As a result, the Si-O bonding particle at an ejection angle of 80° is more than that at an ejection angle of 10°. Furthermore, even though the oxide formation by the OH radical occurs on the surface reaction, the oxide layer is removed by the physical sputtering of the ethanol cluster ion beams.

As already shown in Fig.1, the chemical sputtering of the Si surfaces was enhanced by the ethanol cluster ion irradiation, and the threshold energy for the sputtering was estimated to be approximately 1.5 keV. For the chemical sputtering, the dissociation of an ethanol molecule is of significant importance to produce various kinds of radicals. In order to study the dissociation process of an ethanol molecule, the First-Principles calculation was performed using the computer software named Materials Studio (Accelrys Co.). Fig. 4 shows the snapshots of impact of an ethanol molecule with different incident energies on the Si(111) surface. The bonding energy for Si-Si bond was assumed to be 2.3 eV. Furthermore, the bonding energy of other bonds such as C-H bond, C-C bond, C-O bond and O-H bond in an ethanol molecule was fixed at 4.3 eV, 3.6 eV, 3.7 eV and 4.8 eV, respectively. As shown in the figure, for the incident energy of 2.87 eV, the ethanol molecule reflects from the Si surface after impact, and the Si surface deforms without breaking the Si-Si bond. When the incident energy increases to 12.0 eV, the ethanol molecule starts to be dissociated into C_2H_5O and H radicals, as shown in Fig. 4(b). The C_2H_5O radical is absorbed to the Si surface, and H atom is desorbed from the surface. For the Si surface, the Si-Si bond is broken, and the defect is produced. At the incident energy of 17.3 eV, more atomic bonds of the ethanol molecule and the Si surface are broken, as shown in Fig. 4(c). The irradiation damage of the Si surface by the ethanol cluster ions is enhanced. These results indicate that there is no irradiation damage at the incident energy below a few eV, and the dissociation of the ethanol molecule requires the incident energy of approximately 12 eV. Taking account of the minimum size of the ethanol cluster ions, which is 100 molecules per cluster, the incident energy of the cluster ions is less than 15 eV per molecule at an acceleration voltage of 1.5 kV. Furthermore, it should be noted from Fig.1 that the chemical sputtering of Si surfaces by the ethanol cluster ion irradiation seems to begin at an acceleration voltage of approximately 1.5 kV. These results indicate that the chemical sputtering is closely related to the dissociation process of the ethanol molecule, and the dissociation starts to occur at an acceleration voltage of approximately 1.5 kV.

4. Discussion

The high-rate sputtering of the Si surfaces by the ethanol cluster ion irradiation can be discussed based on a thermodynamic approach as follows; The entropy S is related to the number of states Ω for a cluster consisting of N particles. It is given by

$$S = k(\log \Omega - \log \Omega_0) \qquad (1)$$

$$\Omega_0 = N!h^{3N} \qquad (2)$$

where k is Boltzmann constant, and h is Planck constant. When the displacement motion of particles as well as the vibration and rotation motions of particles is enhanced, the number of states Ω increases, which results in the increase of the entropy.

On the other hand, the first law of thermodynamics indicates that the total energy is conserved for a cluster with a volume of V. It is described as follows [11];

$$TdS = dE + PdV - \mu dN \qquad (3)$$

where T is the temperature of the cluster, P is the pressure of the cluster, E is the internal energy of the cluster, and μ is the chemical potential. When the cluster impacts on a substrate surface, the high-density energy is deposited locally on the small area of the substrate. As a result, the constituent particles of the cluster are displaced, and they have a component of thermal random energy perpendicular to the incident direction. Also, the displacement of the surface atoms occurs. The interaction of the cluster with the surface atoms is non-equilibrium and non-steady state, which is different from a quasi-static process. However, the vibration motion of particles in the cluster increases with increase of the internal energy transferred from the incident energy of the cluster ion, and the thermal energy of particles in the cluster increases. As a result, the enthalpy of the cluster, which is related to the internal energy as well as the pressure and the volume of a cluster, changes according to the incident energy, and the temperature of the cluster also changes. Rough estimation is that the incident energy of 1 eV corresponds to the thermal temperature of 11,600 K. The MD simulation indicated that the temperature of the cluster impact region was a few tens of thousands degrees, although the substrate temperature was at room temperature [12].

During impact of the cluster, several kinds of chemical products are produced. The rate of chemical reaction (ν) with various kinds of reaction paths is described as follows [13];

$$\nu \propto N \frac{kT}{h} \sum_{i=1}^{n} \exp\left(-\frac{Q_i}{kT}\right) \qquad (4)$$

where T is the temperature of the cluster after impact, $Q_i (i = 1,2,,,,,n)$ is the activation energy for a reaction path (i), and n is the number of all the paths. The equation indicates that the rate of chemical reaction increases with increasing temperature. Furthermore, of all parallel paths of chemical reactions, the one with the lowest energy barrier is the most rapid, and such a chemical reaction occurs preferentially.

When the ethanol cluster ions impact on the Si surfaces, the cluster ions are broken up, and the multiple collisions between ethanol molecules and Si surface atoms occur. As a result, the Si surface atoms as well as the ethanol molecules of the cluster are displaced and vibrated at random state, which corresponds to equivalently-high temperature state. Thus, the incident energy of the ethanol cluster ions is used for heating an impact region of the Si surfaces. Therefore, the thermal vibration frequency of the ethanol molecules, which is expressed by kT/h in Eq.(4), becomes extremely high. On the other hand, the barrier height for the chemical reaction is expressed by Q_i/kT, and it becomes relatively low at higher temperatures. As a result, several reaction paths such as hydride, oxide and hydro-carbide path may be performed almost at the same time even for a very short time by the ethanol cluster ion irradiation. Among the paths, the chemical erosions such as silicon hydride and hydro-carbide are enhanced preferentially, and SiH_x and $Si(CH_3)_4$ are produced as volatile compounds. Therefore, they are the origin of the high rate sputtering by the ethanol cluster ion irradiation. With regard to the oxidation, which is another kind of chemical erosion, the irradiated Si surface becomes thermally stable as a SiO_2 surface. As a consequence, the surface binding energy is higher than that of the unirradiated Si surface, and the chemical sputtering effect decreases. However, the physical sputtering caused by momentum transfer of the impinging cluster ions to the surface atoms occurs, and the oxide layer is removed.

Based on the chemical erosion processes, it is considered that the rate of silicon hydride and hydro-carbide reaction by the ethanol cluster ion irradiation is much larger than that of silicon oxide reaction.

5. Summary

The liquid clusters such as ethanol and water clusters were produced by an adiabatic expansion, and the accelerated cluster ions were irradiated on Si(111) and SiO_2 surfaces at room temperature. The sputtering yield of the Si surface by the ethanol cluster ion irradiation was significantly high. This was ascribed to the chemical erosion and sputtering, in which the silicon hydride and hydro-carbide reaction occurred.   On the other hand, for the water cluster ion irradiation, the momentum transfer of the incident energy was performed on the impact area, and the physical sputtering occurred. Compared with the Ar monomer ion irradiation, the sputtering yield of the Si surface by the water cluster ion irradiation was also higher. Furthermore, the liquid cluster ion beam process exhibited unique irradiation effects such as high-density and high-reactivity irradiation effects, which was not obtained by a conventional wet process.

References

[1] P. Sigmund, Phys. Rev. 184 (1969) 383.

[2] J. P. Biersack, W. Eckstein, Appl. Phys. A34 (1984) 73.

[3] L. Dutkiewicz, R. Pedrys, J. Schon, K. Kremer, Phys. Rev. Lett. 75 (1995) 1407.

[4] E.Taglauer: in P. Sigmund (Ed.), "*Fundamental Processes in Sputtering of Atoms and Molecules*" SPUT 92, 43 (1993) 643.

[5] R. Behrisch, W. Eckstein (Eds.), "*Sputtering by Particle Bombardment*" Springer-Verlag Berlin Heidelberg, 110 (2007) 1.

[6] H. Yasumatsu, T. Kondow, Reports on Progress in Physics, 66 (2003) 1783.

[7] I. Yamada, G.H. Takaoka, Jpn. J. Appl. Phys. 32 (1993) 2121.

[8] G.H. Takaoka, H. Noguchi, K. Nakayama, M. Kawashita, e-J. Surf. Sci. Nanotech. 4 (2006) 473.

[9] G.H. Takaoka, M. Kawashita, H. Noguchi, K. Nakayama, Surf. Coat. Technol., 201 (2007) 8628.

[10] G.H. Takaoka, H. Noguchi, K. Nakayama, Y. Hironaka, M. Kawashita, Nucl. Instrum. Methods B237 (2005) 402.

[11] R.P. Feynman, R.B. Leighton, M.L. Sands, "*The Feynman Lectures on Physics*" Addison-Wesley Publishing Co. Inc., Vol.2 (1965) Chaps.19 and 20.

[12] Z.Insepov, I.Yamada, Surf. Rev. Lett. 3 (1996) 1023.

[13] W.D.Kingery, H.K.Bowen, D.R.Uhlmann, "*Introduction to Ceramics*" John Wiley & Sons Inc., New York, 1976, Chap. 9.

Figure Captions

Fig. 1: Dependence of sputtered depth for Si(111) and SiO_2 surfaces on acceleration voltage

for ethanol and water cluster ions.

Fig. 2: Depth profiles of (a) O1s and (b) C1s peaks for the Si(111) surface irradiated at an

acceleration voltage of 9 kV by the ethanol cluster ion beams.

Fig. 3: Si2p peaks for the particles released at an ejection angle of (a) 10 ° and (b) 80° by the

ethanol cluster ion irradiation.

Fig. 4: Snapshots of impact of an ethanol molecule with an incident energy of (a) 2.87 eV, (b)

12.0 eV and (c) 17.3 eV on the Si(111) surface.
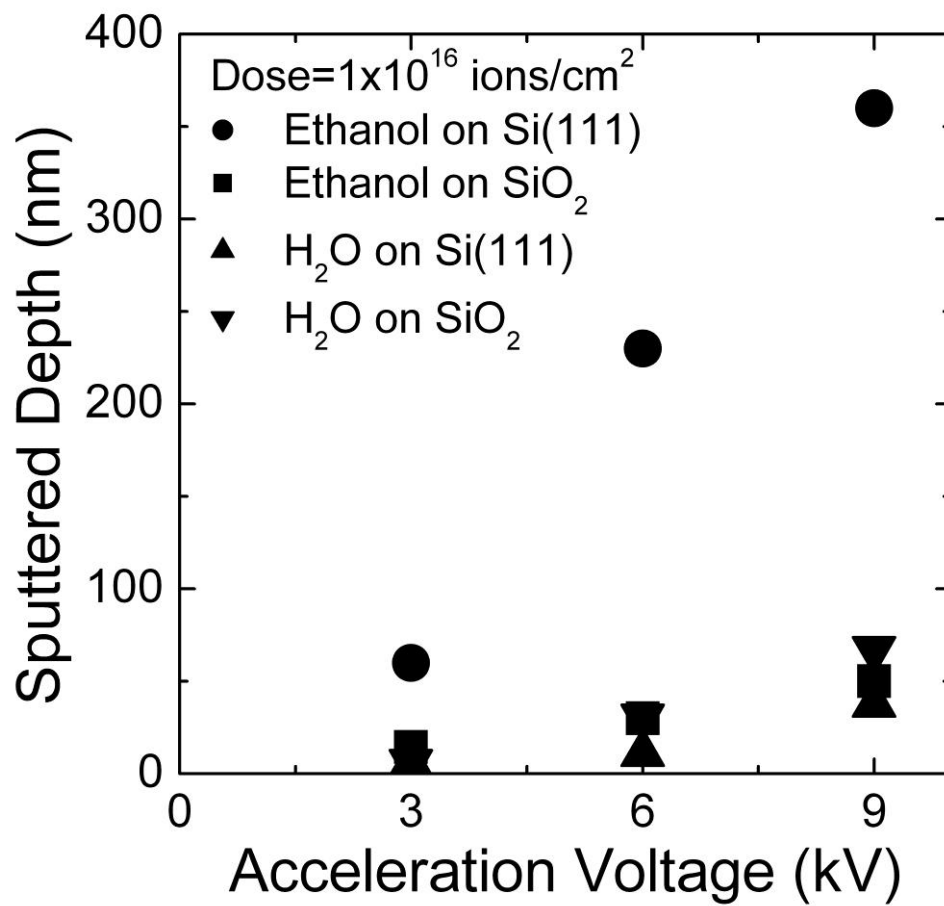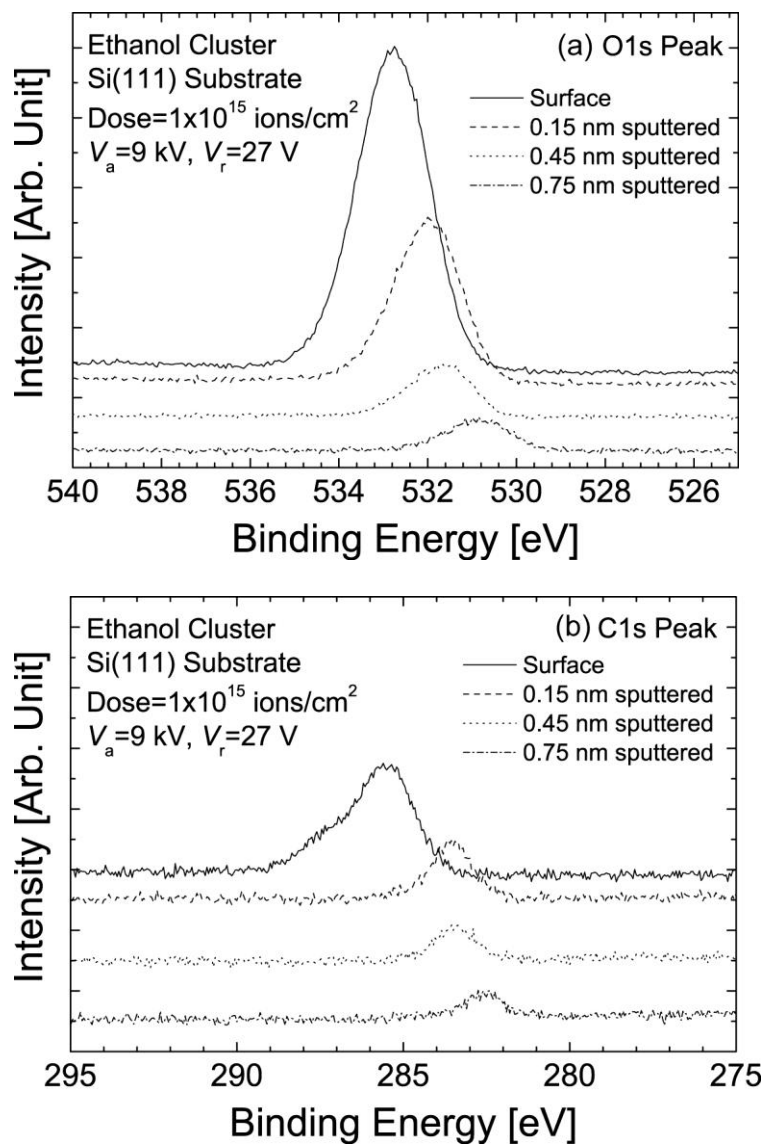
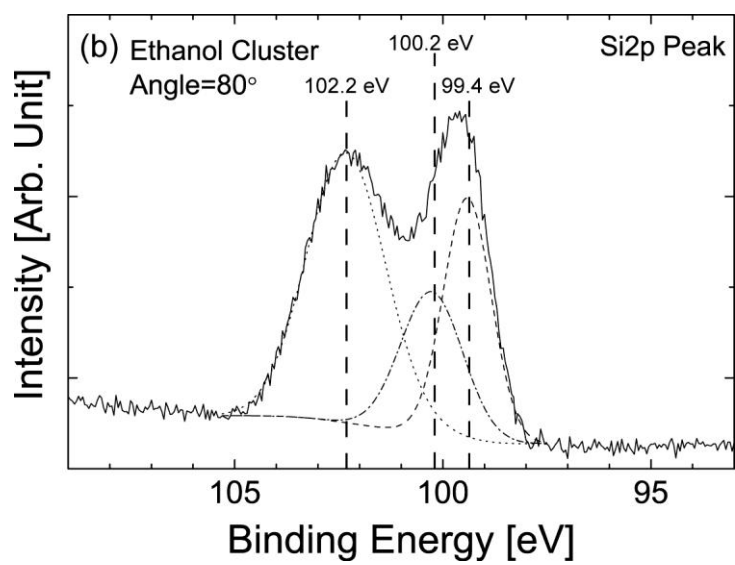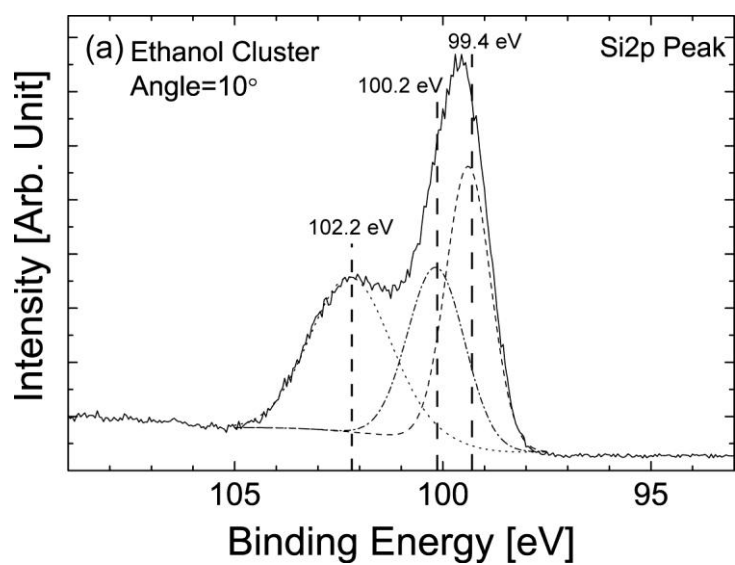Figure 1: Takaoka et al.
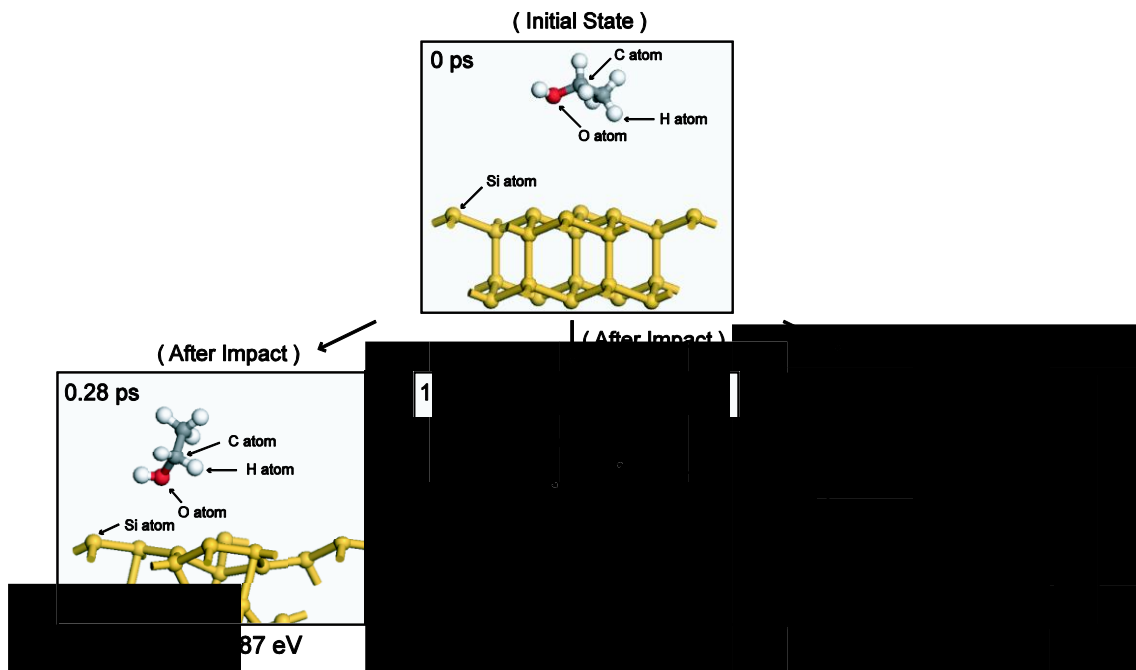
Figure 2: Takaoka et al.

Figure 3: Takaoka et al.

(Initial State)

0 ps

C atom

O atom

H atom

Si atom

(After Impact)

0.28 ps

C atom

H atom

O atom

Si atom

(After Impact)

87 eV

Figure 4: Takaoka et al.