Applied Surface Science 279 (2013) 171–179

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Study on preparation method for short-chain alkylsiloxane self-assembled monolayers and the diffusion behavior of copper on silica surfaces

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ARTICLE INFO

Article history:
Received 7 November 2011
Received in revised form 6 April 2013
Accepted 17 April 2013
Available online 23 April 2013

Keywords:
Self-assembled monolayers (SAMs)
Preparation method
Alkylsiloxane
Copper
Diffusion behavior

ABSTRACT

The properties of self-assembled alkylsiloxane on hydroxylized silica surfaces were studied to explore the preparation method of the short-chain self-assembled monolayers (SAMs), and the diffusion behavior of copper on the SAMs was also investigated using molecular dynamics (MD) simulation method. Six models were built on four kinds of silica crystalline planes to form different interface bonding modes. The influences of bonding modes, chain lengths and terminal groups on the thickness, packing, morphologies and roughness of the SAMs were studied to analyze the relationships between these factors respectively and the stability of the SAMs. The results show that the thickness values of the SAMs with cross-linking mode are similar to the experimental values, and are much greater than those of the single-linking SAMs. For single-linking systems, long-chain SAMs are more ordered than short-chain SAMs, while for cross-linking systems, short-chain SAMs are more ordered. Terminal groups are of little influence on packing and surface morphology. In the systems studied, 2-methylene SAMs could perfectly be formed on α-quartz (1 0 0) surface in a cross-linking mode. The copper diffusion behavior on this surface was also studied for the ordered short-chain SAMs might be promising diffusion barriers for copper connections in the ultra-large-scale integrated circuit fabrication in the future.

1. Introduction

Self-assembled monolayers (SAMs) have experienced huge growth in recent years as a new class of functional materials in heterogeneous catalysis, biosensing, semiconductor fabrications and in other fields. There are several forms of SAMs, alkanoic acids chemically adsorbed on metal oxide surfaces, alkanethiols on metal surfaces, and alkyltrichlorosilane or alkylsiloxane on hydroxylated surfaces, etc. Because alkylsiloxane SAMs can be bonded on silica surfaces and used as diffusion barriers for copper connections in the ultra-large-scale integrated circuit (ULSI) fabrication, great progress has been made since they were introduced in the 1980s and 1990s of the last century.

Studies of alkylsiloxane/silica SAMs in ULSI fabrication have proven that the SAMs can act as a perfect barrier at a thickness of less than 2 nm [1–5]. In the work of Ganesan et al. [2], they found the carboxyl-terminated SAMs at the Cu/SiO_2 interface could give rise to the increase of the copper diffusion-induced device failure time by a factor of 12 compared to the interfaces without a SAM barrier. As the size of semiconductor device shrinks, short-chain alkylsiloxane/silica SAMs might be a promising alternative of traditional diffusion barriers for copper in the ULSI. However, it is well known that, short-chain SAMs are not as stable as long-chain SAMs.

In order to prepare uniform and ordered short-chain alkylsiloxane SAMs on hydroxylated Si/SiO_2 surfaces, one should clearly understand the mechanism of SAM formation. There are three steps involving SAM formation [6,7]: (1) the $-Si(OCH_3)_3$ head groups are hydrolyzed to $-Si(OH)_3$ groups, (2) the head hydroxyl groups are dehydrated when aggregated with the hydroxyl groups of the surface, and (3) the residual hydroxyl groups of the interface condense to form ordered assembled monolayers. The CN- and NH_2-terminated SAMs with 3-methylenes have been prepared by Nitzan et al. [8]. We also prepared COOH-terminated SAMs with 2-methylenes from the hydrolysis of CN-terminated SAMs [9].

Research using computational simulation method provides much essential information regarding the fabrication and stability of the SAMs from a microscopic perspective. Stevens [10] pointed out that the van der Waals (vdW) diameter for C atoms is 3.5 Å, which is greater than the maximum distance between Si atoms of the Si—O—Si cross-link, 3.2 Å; and therefore, it has been shown that cross-polymerization is unlikely to occur for alkylsiloxane monolayers at full coverage because the distance is much shorter than the vdW diameter, which implies that the C atoms are overlapped.

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http://dx.doi.org/10.1016/j.apsusc.2013.04.064

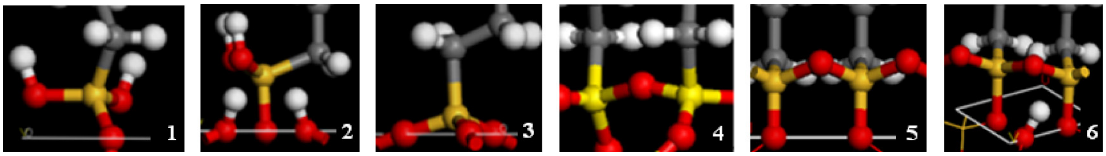

Fig. 1. Interface models of SAMs used in the simulations.

Yamamoto et al. [11] investigated the bonding network of octadecylsilane SAM/SiO_2 on hydroxyl-terminated cristobalite (1 0 0) or (1 1 1) substrate by means of molecular simulations. Their simulation results have revealed the increment of the Si—O—Si bond density disordering the molecular packing. Since cross-linking in alkylsiloxane monolayers has been considered to play a role in stabilizing, we considered that, the stability of SAMs results from various interactions. The properties of SAMs are influenced by many factors, including hydroxyl distribution on the substrate surface, connection modes, terminal groups and the chain length of the alkylsiloxane, etc. In order to find the stability factors and the preparation method of short-chain SAMs, six systems of alkylsiloxane SAMs with different terminal groups and different chain length assembled on different silica crystalline planes were optimized to analyze the influence of these elements on the SAMs properties. On the basis of the above research, copper diffusion behavior was also investigated on the short-chain SAMs using molecular dynamics (MD) simulation method.

2. Experimental methods

2.1. The models

The alkylsiloxane/silica self-assembled monolayers are prepared by dipping samples into organic solution of alkylsiloxane. The presence of water has great effect on the quality of the SAMs. Here, in order to investigate the influence of other factors on the monolayer, an ideal state with alkylsiloxane assembled on the silica surface was considered and the systems contain no water.

The substrates used in the experiments mostly are amorphous SiO_2. It is difficult to estimate the hydroxyl distribution. In the simulations, crystalline planes of silica were usually used as substrates. The most commonly studied forms of silica are β-cristobalite (1 1 1) and α-quartz (1 0 0) [1–3,11]. The substrates chosen in this work are β-cristobalite (1 1 1), β-cristobalite (1 0 0) and α-quartz (1 0 0) crystalline planes. The surfaces are obtained by cutting the upmost layer of O atoms, then CN- and COOH-terminated SAMs with different chain lengths (with 2-, 6- and 11-methylene) are chemically adsorbed on them forming different interface structures. The six unit cell models are described in Fig. 1 and Table 1. The 8 × 8 systems were used in the simulation process.

In model 1, the O atom of this layer is bonded to the Si atom of the alkylsiloxane forming a full coverage of $Si(OH)_2(CH_2)_nCN$ or $Si(OH)_2(CH_2)_nCOOH$ monolayer with two residual head hydroxyl groups in the interface. The bond length of Si—O is 1.650 Å, while the minimum distance of the O atoms of adjacent surface hydroxyl groups of this model is 4.385 Å. So, model 1 must take the single-linking mode because the distance between O atoms is much longer than that between Si atoms of Si—O—Si cross-link bonds. In model 2, one atom of the three O atoms of this layer is bonded to the Si atom of the alkylsiloxane chain forming monolayer that contains two head hydroxyl groups and two surface hydroxyl groups in the interface. In model 3, three O atoms of this layer are bonded to the Si atom forming anchor-like monolayer. These three models are in the single-linking bonding mode. In models 4 and 5, each O atom is bonded to one Si atom, forming a cross-linking monolayer. In model 6, two O atoms of the three O atoms are bonded to the Si atom, forming a cross-linking monolayer and with a surface hydroxyl group in the interface.

2.2. Simulation details

The molecular dynamics simulations were performed with Tinker-Linux 5.0 package [12] in conjunction with the VMD visualization program [13]. The OPLS all-atom (OPLS-AA) force field [14] and its extension for crystalline silicon oxide [15] were employed to describe the chains and interactions within the monolayer coated surface respectively. The parameters for the interactions of copper and SAMs were optimized based on the universal force field (UFF) [16]. The three-dimensional periodic boundary condition (PBC) was applied to the simulation systems, and the size of the PBC was exactly fit the crystal size in *x*- and *y*-direction and the connection information is given to form an infinite SAM surface. The simulations were performed in an isothermal and isobaric (NPT) ensemble. The Berendsen algorithm was employed to keep the temperature and pressure at 298 K and 101.3 kPa, respectively. A cutoff distance of 12 Å was used for accurate computation of the Lennard–Jones interactions. All the systems were flexible during the simulations. After initial equilibration, the whole system was carried on a 1 ns MD simulation with the time step of 2 ps.

3. Results and discussion

3.1. Equilibration of the systems

Two criterions have been adopted to evaluate whether the simulation system achieved equilibrium, which is the potential energy [17,18] and the root mean-square deviation (RMSD) [19] of the system. The plots of RMSD with respect to simulation time are shown in Fig. 2.

Table 1
The interface models of SAMs for one unit cell.

	Model (unit cell)					
	1	2	3	4	5	6
Crystalline plane	β-(1 1 1)	β-(1 1 1)	β-(1 1 1)	α-(1 0 0)	β-(1 0 0)	β-(1 1 1)
Surface size (Å)	4.385 × 5.063	4.385 × 5.063	4.385 × 5.063	4.913 × 5.405	5.063 × 5.063	4.385 × 5.063
Number of hydroxyl	1	3	3	2	2	3
Number of chain	1	1	1	2	2	2
Area per chain ($Å^2$)	22.19	22.19	22.19	13.28	12.82	11.10
Number of residual hydroxyl	2	4	0	0	0	1
Linking mode	Single	Single	Single	Cross	Cross	Cross