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APPLICABILITY OF ALKYL MONOLAYERS ON Si(111) TOWARDS PRACTICAL NANO-SCALE FABRICATION

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Abstract. A novel process of electron-beam nanometer-scale fabrication on Si(111) wafer surfaces has been proposed on the basis of application of alkyl monolayers as the patterning media. The alkyl (C_nH_{2n+1}-) monolayers prepared with the Grignard reagents were subjected to electron-beam patterning with ambient O_2 and deposition of metals onto the formed patterns by immersion into aqueous solutions containing metal ions. The tolerance of alkyl-covered Si(111) surface towards aqueous solutions has been demonstrated. The alkyl monolayer survived in Cu deposition solution containing HF, even while a visible amount of Cu deposit was built up.

1. INTRODUCTION

The fabrication of nanometer-scale structures and application of nano-particles for practical purposes are nowadays the key issues in the field of micro-engineering. Among various kinds of development, the fabrication of desired nanometer-scale 2-dimensional patterns over solid substrates is the fundamental prerequisite for most of engineering applications.

Our original mission was to develop an entire process to prepare a 2-dimensional array of nano-dots (a few tens of nm in diameter) spaced with a few tens of nm over silicon wafer surfaces. This type of nano-dot arrays was supposed to be used as an ultrahigh-density data storage medium placed in vacuum with a facility for writing and reading by a fine scannable electron beam. The application of scanning probe methods for nano-patterning has been frequently reported [1] to achieve the ultimate spatial resolution of the angstrom order. However, scanning probe methods are usually limited in a narrow scan range, and the speed of dot patterning is not satisfactory. Today, a fine focused electron beam with a full-width-at-half-maximum diameter about 10 nm is available by field-emission electron source and magnetic-field focusing [2], and can be scanned over an extended area rapidly.

Then we are in need of the patterning media that are viable in the scale of nanometer, robust enough for the processes of pattern developing, and sensitive enough for electron beam to realize very rapid pattern writing. We focused our attention to Si surfaces covered by a monolayer material, which can drastically alter the chemical reactivity of Si surfaces. Since the thickness is limited to one monolayer, there is virtually no depth profile, and we can eliminate the problems of focal depth of electron beam and diffusion within the resist layer in making ultimately small patterns [3-7]. This is the motivation to investigate the nature of organic monolayers formed on Si(111) surfaces. Our strategy for fabrication of 2-dimensional nanoscale patterns is formulated as follows:

(1) Deposition of a monolayer of organic molecules covalently bonded on surface Si atoms.
(2) Drawing nanometer-scale patterns by altering the monolayer by a fine electron beam.
(3) Selective deposition of metal atoms onto the bombarded portions.

Process (2) corresponds to the "writing" procedure by electron beam. Process (3) is important as

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heavy metal atoms, even in an amount of one monolayer or less, will differentiate the absorbance and reflectivity of electrons from the portions without deposit. This will facilitate the “reading” procedure as recording media.

As a benchmark test, all of these processes were successfully put into practice by using an electron beam with a diameter of 1 mm [8,9]. The previously reported preparation method of alkyl monolayers (CH_3- to $C_{18}H_{37}$-) [10] was verified on the basis of surface analysis by Auger electron spectroscopy (AES), infrared internal-reflection absorption spectroscopy and scanning tunneling microscopy (STM). As for electron-beam patterning, introduction of low-pressure O_2 gas during bombardment facilitated the analysis of bombarded portions by the formation of SiO_2, and this SiO_2 adlayer was utilized in the succeeding processes. Upon brief immersion into an aqueous solution of $NiSO_4$ + $(NH_4)_2SO_4$ at room temperature, Ni was impregnated only over the bombarded portions, detected by AES. This is due to the contrast of the reactivities of SiO_2 adlayer and alkyl adlayer towards Ni^{2+} ions.

This short paper reports the results on two key issues involved in the above-mentioned scheme of nano-patterning method:

(1) How robust is the alkyl monolayer on Si(111) against treatment in aqueous solutions?

It is known that the hydrogen-terminated H:Si(111) is easily oxidized even in purified water because of the existence of dissolved O_2 from the atmosphere [11]. Alkyl-covered Si(111) has been compared to H:Si(111) by contact to pure H_2O.

(2) How tolerant is the alkyl monolayer on Si(111) in the process of metal deposition in the solutions including powerful reagents, such as hydrofluoric acid (HF)?

This question has been answered by actually performing deposition of Cu in a $CuSO_4$ + HF + NH_4F solution (“BHF” solution) onto the electron-bombarded portions. The alkyl monolayer survived even while metallic Cu was deposited to build up a thick layer even visible to eye.

2. EXPERIMENTAL

The detailed procedures of pre-treatment of Si(111) wafers (*n*-type, 3~8 Ω×cm) in a hot H_2O_2+H_2SO_4 solution and hydrogen-termination in 40% NH_4F were described elsewhere [8,9]. Preparation of decyl (*n*-$C_{10}H_{21}$-) layers by Grignard reagents were performed by the method reported by Boukherroub et al.[10] We used a commercial $(C_2H_5)_2O$ solution of *n*-decylmagnesium bromide (*n*-$C_{10}H_{21}$MgBr, Aldrich Chemicals). The reaction was performed at 35 °C for 18 hours. Surface elementary analysis by AES and electron-bombardment patterning were done in an ultrahigh vacuum (UHV) chamber equipped with a cylindrical mirror analyzer (CMA, with a coaxial electron gun), an electron gun for electron bombardment, and a two-stage load-lock sample introductory system. To deposit Cu over the electron-bombarded spots, an aqueous “BHF” solution composed of 0.01 *M* $CuSO_4$ + 0.11 *M* HF + 0.11 *M* NH_4F was prepared. Scanning electron microscopy (SEM) was performed by a Hitachi S4500S field-emitter-type microscope.

3. RESULTS AND DISCUSSION

The robustness of $C_{10}H_{21}$:Si(111) surface was evaluated under comparison with the H:Si(111) surface by tracing adsorbed oxygen in pure H_2O. H:Si(111) and $C_{10}H_{21}$:Si(111) were simply immersed in Milli-Q water stored in a teflon container with the lid off for one day or more. The concentration of O_2 dissolved is supposed to be equilibrated with the atmosphere. The samples were removed from pure H_2O and subjected to AES.

After immersion, Auger spectra of these two surfaces consisted of the signals of Si, C and O. Fig. 1

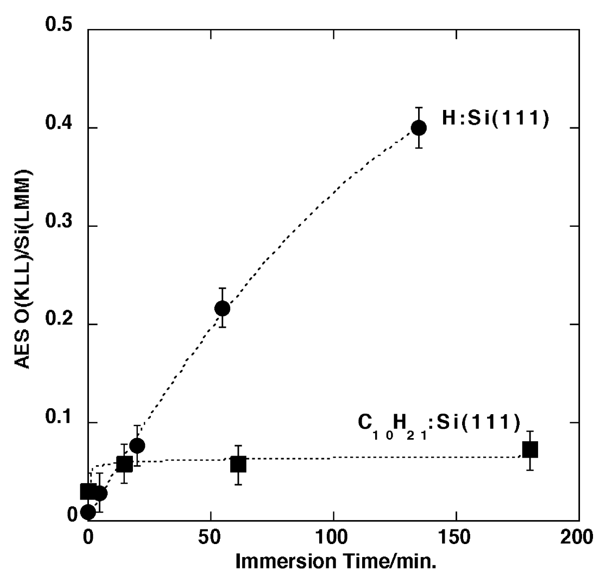

Fig. 1. Auger peak height ratio O(KLL, 520 eV)/Si(LMM, 100 eV) of H:Si(111) and $C_{10}H_{21}$:Si(111) as a function of the immersion time in pure H_2O exposed to the atmosphere. H:Si(111) was prepared by immersing pre-oxidized n-Si(111) in a 40% aqueous NH_4F solution for 10min. $C_{10}H_{21}$:Si(111) was prepared by the reaction of H:Si(111) and *n*-$C_{10}H_{21}$MgBr (1 M in diethylether) at 35 °C for 18 hours. Incident electron energy for AES = 2 kV.

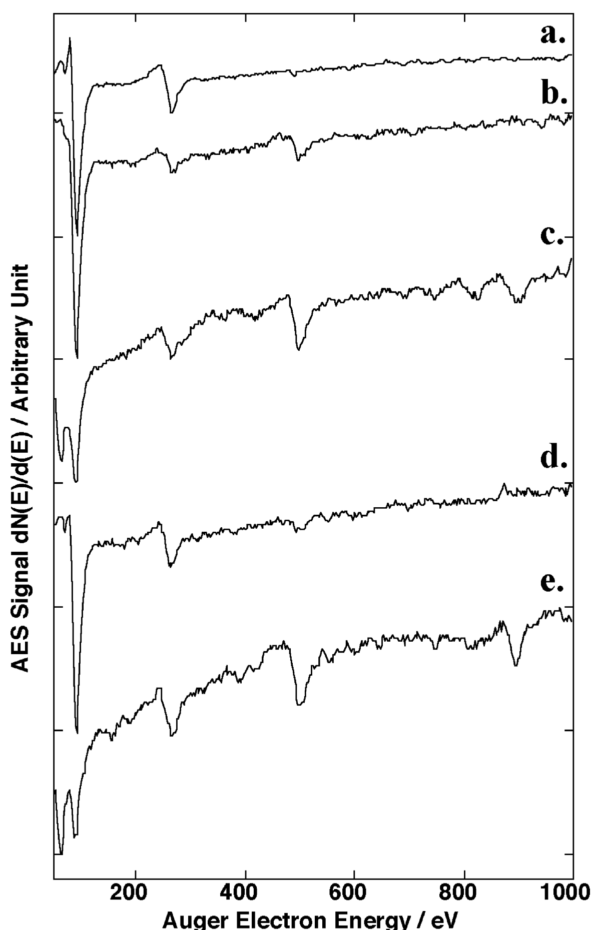

Fig. 2. AES of $C_{10}H_{21}$:Si(111) in the process of electron bombardment and Cu impregnation. The spectra were recorded at 2 kV of the incident. (a) Newly prepared $C_{10}H_{21}$:Si(111). (b) After electron bombardment (incident electron energy = 2 keV sample current = 100 mA, beam spot diameter = ca.1 mm, irradiation time = 300 seconds) with ambient O_2 ($4 \cdot 10^{-4}$ Pa) recorded at the spot center of bombardment. (c) After immersion of the specimen of (b) into the 0.01 *M* $CuSO_4$ + 0.11 *M* HF + 0.11 *M* NH_4F solution at room temperature for 5 seconds and rinsing in ultrapure water, recorded at the spot center, and (d) 3 mm away from the center. (e) After immersion in the same solution for 30 seconds and rinsing in ultrapure water.

shows the Auger peak height ratio O(KLL, 520 eV)/ Si(LMM, 100 eV) of H:Si(111) and $C_{10}H_{21}$:Si(111) as a function of the immersion time in pure H_2O. It is obvious that H:Si(111) is rapidly oxidized, and is oxidized continuously, whereas $C_{10}H_{21}$:Si(111) bears a small amount of O in the initial stage and no increase of O is seen in the extended period. On H:Si(111), the peak position and the fine structure of Si(LMM) transition were gradually altered to those of silicon oxide. On the other hand, the Si(LMM) peak remained unchanged on $C_{10}H_{21}$:Si(111) for all of the immersion times.

It is concluded that the substrate of H:Si(111) is oxidized in pure water dissolving O_2 equilibrated with the atmosphere to form SiO_2, and that the substrate of $C_{10}H_{21}$:Si(111) is not oxidized. The O signal seen in the $C_{10}H_{21}$:Si(111) spectra is probably due to H_2O trapped in the brush-like adlayer composed of linear $C_{10}H_{21}$- chains, or due to slight partial oxidation of $C_{10}H_{21}$- admolecules. The oxidation of substrate Si is considered to be the effect of dissolved O_2^- in H_2O [11]. This result impressively indicates that the robustness of alkyl-covered Si(111) is essentially distinguished from that of H:Si(111).

The entire process of electron-beam bombardment and deposition of Cu in the “BHF” solution was traced step by step by AES, shown in Fig. 2. The starting $C_{10}H_{21}$-covered Si(111) (spectrum a.) was subjected to electron-beam bombardment. Spectrum b shows formation of an oxidized portion. This bombarded specimen was immersed in the $CuSO_4$ + HF + NH_4F solution for just 5 seconds at room temperature. Spectra c and d indicate the contrast of Cu(LMM) Auger signal from the detection areas on and off the electron-bombarded spot.

Though the Cu(LMM) signal in spectrum c looks small, it corresponds to an amount larger than a monolayer. Spectrum e was recorded at the spot of bombardment after 30 seconds’ immersion in the BHF solution. A visible Cu spot was seen at the center of bombardment on the specimen. Spectrum e is practically of the surface of bulk Cu metal, and Spectrum c is close to that. This process of segregation of bulk Cu metal on Si surface is considered to involve the dissolution of Si into SiF_6^{2-} and coupled reduction of Cu^{2+} into metallic Cu [12,13] in this BHF solution. Dissolution of SiO_x on the bombarded area precedes Cu segregation, and the alkyl-covered portions are intert.

The apparent contrast of the Cu deposit and the un-deposited part was magnified by SEM, as shown in Fig. 3. The image of the border of the electron-bombarded spot clearly demonstrates that the alkyl monolayer is resistive for the treatment in solutions such as BHF. The average grain size of Cu deposit is well over 50 nm. Our target dimension of the dots is 10 nm in diameter and 1 monolayer in thickness, and the present deposited layer does not match our purpose. In general, dispersed impregnation of metal ions into the oxidized silicon layer from dilute solutions is probably preferable, as it will not compose metallic grains of large size. This experiment is just to demonstrate how robust the alkyl monolayers are.

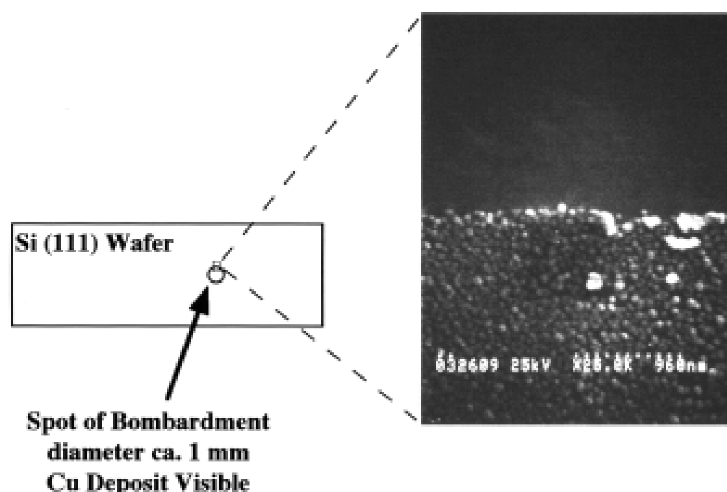

Fig. 3. An image of patterned Cu deposit by scanning electron microscopy. The $C_{10}H_{21}$:Si(111) surface was subjected to electron bombardment (incident electron energy = 2 keV sample current = 100 mA, beam spot diameter = ca.1 mm, irradiation time = 300 seconds) with ambient O_2 ($4 \cdot 10^{-4}$ Pa), and immersed into the 0.01 *M* $CuSO_4$ + 0.11 *M* HF + 0.11 *M* NH_4F solution at room temperature for 30 seconds and rinsing in ultrapure water. The spot pattern composed of Cu metallic deposit was clearly visible, and a part of the border was magnified by SEM (incident electron energy 25 kV).

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