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In-Situ Observation of Silicide Formation on Hydrogen-Terminated Si Surface by UHV-STM and LEED

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Initial stage of silicide formation were investigated for both titanium and nickel on H-terminated Si (111)-1x1 surface, and comparisons were made between on Si(111)-7x7 surface. In the case of H-terminated surfaces, islands structure was stable at temperatures below 500℃ which almost corresponded to a desorption temperature of Si-monohydride. On the other hand, strong interaction between metal atoms and Si were observed below this temperature on Si (111)-7x7 surface. There is a drastic change in islands growth mode of titanium silicide at 500℃. There is no growth of Ti islands below 500℃ due to a stable H-Si bonding, and a rapid growth which corresponds to titanium silicide formation occurs above 500℃.

1.Introduction

Demand of higher speed operation of Si ULSIs brings about necessity of silicide technology in a sub micron scale. In this situations, precise control of aggromelation and phase transition temperatures is becoming a serious issue since these phenomena are delicately dependent on substrate precleaning method [1]. The present work investigates an effect of hydrogen (H-) termination of Si substrate on agglomeration and formation of silicide by usage of in-situ UHV-STM and LEED , and a comparison has been made between on H-terminated Si(111)-1x1 and on Si(111)-7x7 reconstructed surface.

2.Experimental Method

H-terminated Si(111)-1x1 was prepared by either dipping in 40% NH_4F after removal of organic compounds (wet treatment), or adsorption of atomic hydrogen in a vacuum environment at 400℃ (dry treatment). In the latter case, at first Si substrate was heated up to 1000℃, then atomic hydrogen was introduced in the vacuum chamber. On the other hand, Si(111) -7x7 reconstructed surface was prepared by direct current heating up to 1200℃. Pure Ti or Ni of less than a few atomic layers was deposited by evaporation in a high vacuum which pressure was lower than $1x10^{-7}$ Pa, then STM and/or LEED observations and annealing were carried out alternately. Annealing temperatures were changed to higher ones, successively.

3.Nickel silicide formation

Figure 1 shows STM image of H-terminated Si (111)-1x1 surface prepared by dry treatment. A clear 1x1 structure with 3-fold symmetry of Si-monohydride is observed in most part of the surface [2], however, line shape defects and many mono-layer height islands are observed [3]. It is considered that most of Si atoms which constitute these islands came from ad-atoms of

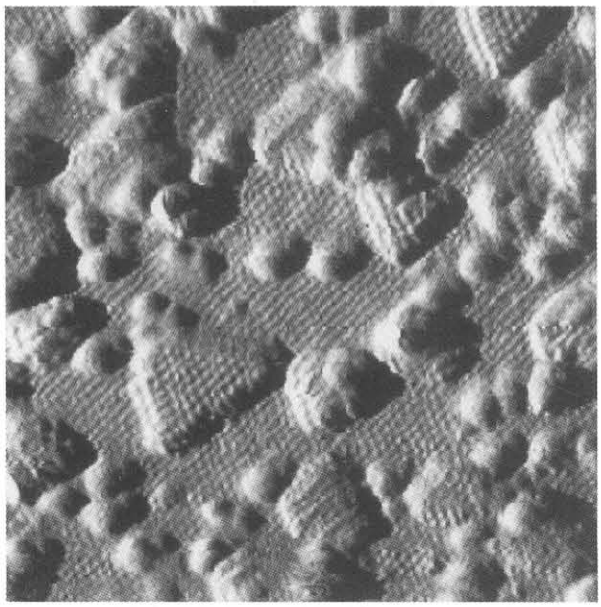

Fig.1 UHV-STM observation of H-terminated Si(111) surface by dry treatment. 20x20nm

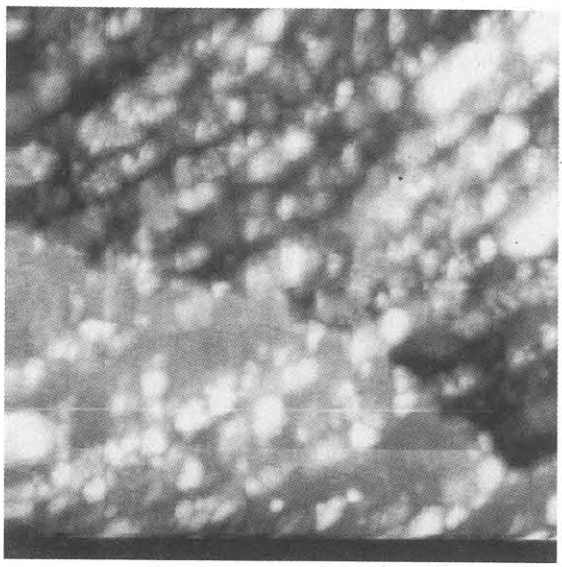

Fig.2 UHV-STM observation of Ni-deposited Si(111) substrate annealed at 400℃ which was H-terminated by dry treatment. 50x50nm

Si(111)-7x7 reconstructed surface. Islands which are larger than 4nm have a clear [111] perimeter and 1x1 periodicity. On the other hand, islands which are smaller than 3nm have a round shape and there is no surface periodicity.

Next mono layer of Ni was deposited on this surface. Ni islands were randomly distributed at the room temperature, and they were stable even after 400℃ annealing as shown in Fig.2. In the case of Si(111)-7x7 surface, islands were formed on unfaulted half of 7x7 cell at room temperature, and they were periodically arranged. When Ni deposited Si(111)-7x7 surface was annealed at 400℃, domain structure of nickel silicides which consists from $\sqrt{3} \times \sqrt{3}$ and $\sqrt{19} \times \sqrt{19}$ was formed as shown in Fig.3 [4]. It is suggested that Ni clusters are stable and never reacts with Si at 400 ℃ on H-terminated surface since monohydride on Si is stable up to 450℃ [5].

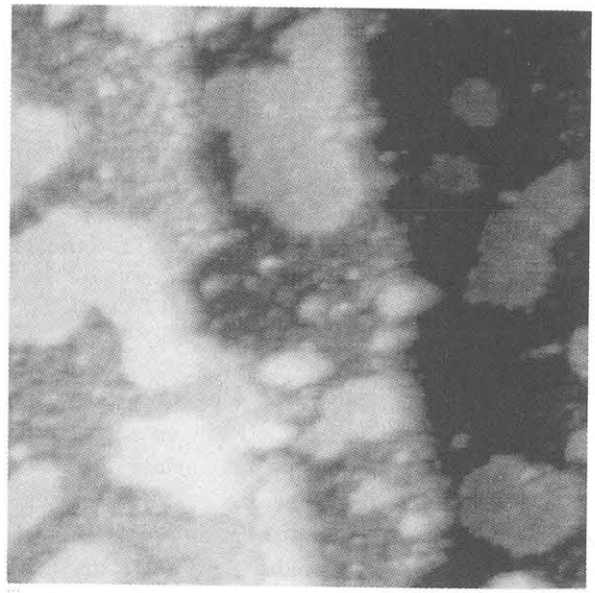

Fig.3 UHV-STM observation of Ni-deposited Si(111) substrate annealed at 400℃ which had 7x7 structure before deposition. 50x50nm

4. Titanium silicide formation

Figure 4-(a) shows STM observation of H-terminated Si (111) surface by wet treatment [6] on which 1/2 layer of Ti was deposited at a room temperature. Ti islands of 1- 3nm were distributed randomly on the Si(111)-1x1 surface. This structure was not changed up to 500 ℃, which almost corresponded to the desorption temperature of H of Si mono-hydride [5], and these islands never grew. On the other hand, STM image of Ti islands formed on Si(111)-7x7 surface is shown in Fig.4-(b). A clear 3-fold symmetry which reflects underlayer 7x7 structure was observed by FFT analysis. Thus Ti islands were formed on unfaulted or faulted half of (7x7) even at a room temperature. A gradual growth of islands by annealing was observed at temperatures below 500℃, and a rapid growth occurred above 500℃.

By annealing at temperatures higher than 600℃, (1x1) surface became unstable and Si(111)-7x7 structure appeared, and islands grew drastically (Fig.5). LEED analysis strongly suggests that islands are Ti crystals when temperature is lower than 500℃, and they changes to $TiSi_2$ when it is higher than 500℃. Average islands volumes are shown as a function of a reciprocal temperature (Fig.6). Drastic islands growth were observed for both cases at temperatures higher than 500℃, which may corresponds to $TiSi_2$ formation. However, there is a small difference in the activation energies. It is suggested that there is still an effect of hydrogen on silicidation kinetics even though there is no silicon-hydride.

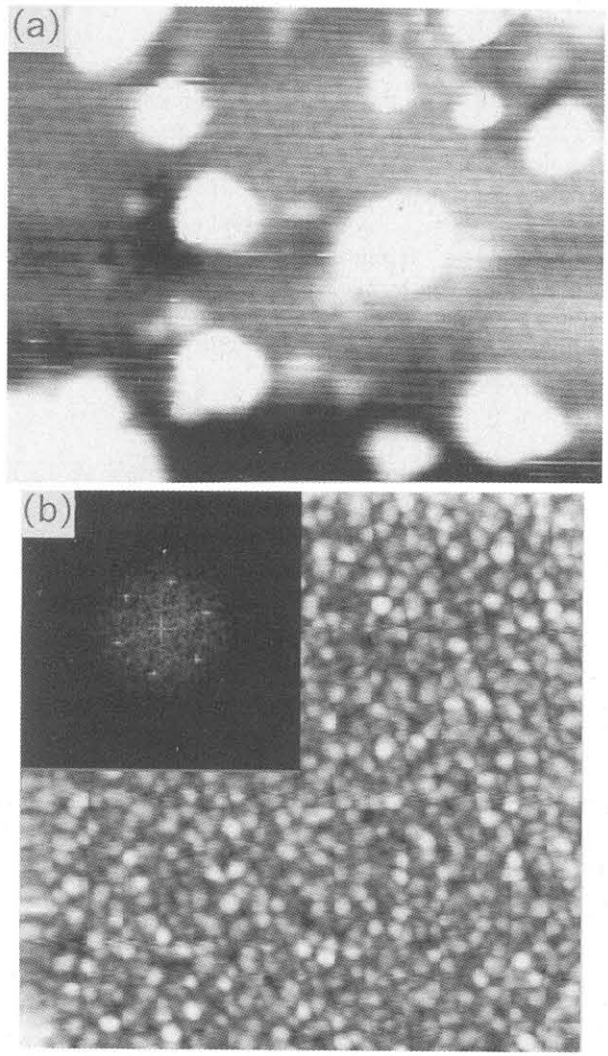

Fig.4 UHV-STM observation of Ti-deposited Si(111) surface at a room temperature.
(a) on H-terminated Si(111) by wet treatment. 10x8nm
(b) on Si(111)-7x7. 25x25nm

5.Conclusions

Initial stage of silicide formation were investigated for both titanium and nickel on H-terminated Si (111)-1x1 surface. Islands structure were stable for both metals at temperatures below 500℃ which almost corresponded to a desorption temperature of Si-monohydride. On the other hand, interaction

between metal atoms and Si were observed below this temperature on Si (111)-7x7 surface. The difference is peculiarly shown in the case of nickel such that domain structures of NiSi was observed at 400℃ on Si (111)-7x7.

It is shown that there is a drastic change in islands growth mode of titanium silicide at about 500℃. There is no growth of Ti islands at temperatures below 500℃ due to a stable H-Si bonding, however, a drastic growth occurs concomitant with initiation of titanium silicide formation.

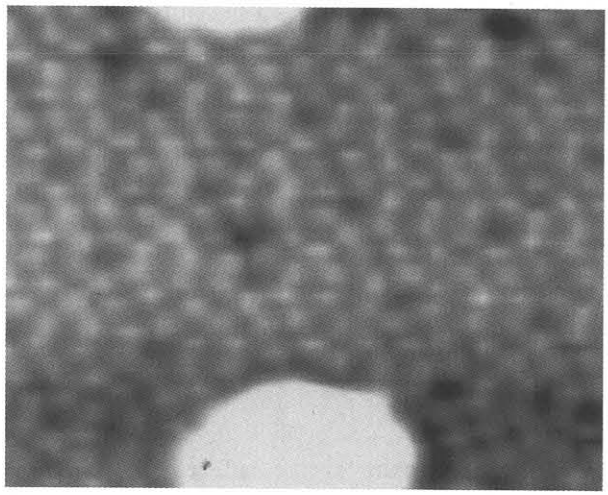

Fig.5. UHV-STM observation of Ti-deposited Si(111) surface annealed at 760℃. 10x8nm

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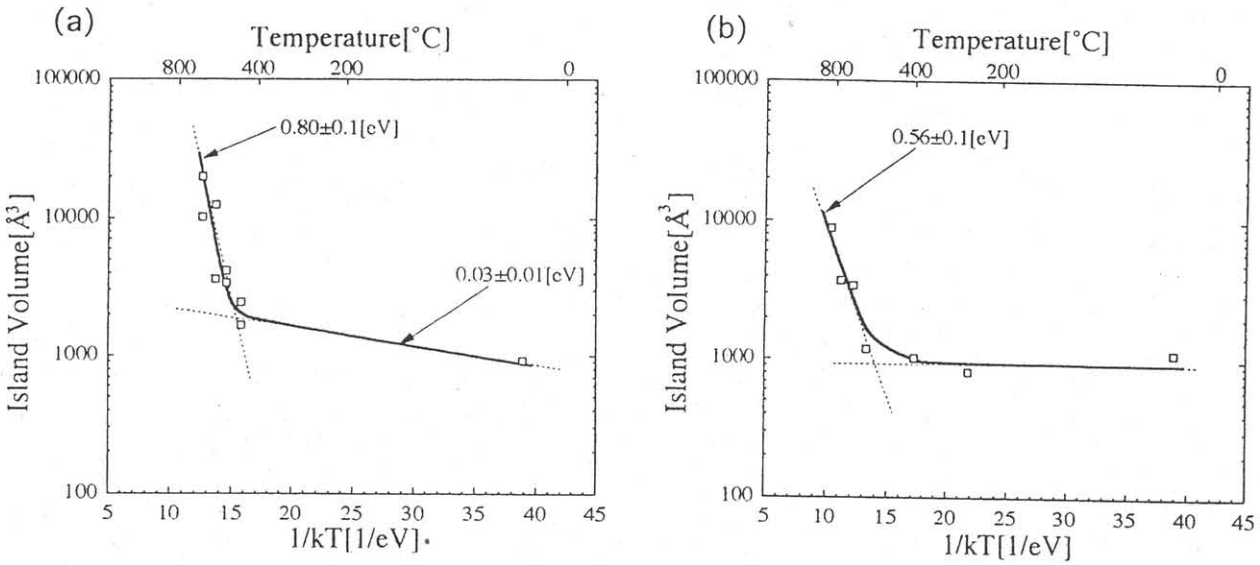

Fig.6 Islands volume as a function of reciprocal of temperature. (a) on Si (111)-7x7 , (b) on H-terminated Si(111)-1x1.