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Atomistic Observation of Titanium Adsorption and Initial Growth of Titanium Silicide on Si(111)

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Abstract

The nucleation and initial growth of titanium silicide on Si(111)7×7 surface structure has been studied using scanning tunneling microscope. At room temperature the deposited Ti atoms coalesce to form the islandlike cluster with the increase of the Ti coverage. Annealing drives the growth of plate structure from island structure. The plate structure's top is flat and their height is almost twice of that of step-height. The growth direction of platelike titanium silicide is reflected by the underlying Si surface structure.

1 Introduction

With the miniaturization of device in integrated circuits, the incorporation of metal silicide has been intensively considered to solve the problem of increasing resistance. Among metal silicides, titanium silicide has been extensively studied because of its lowest resistivity among all silicides and good high temperature stability.

The formation and growth of titanium silicide has been extensively investigated using various kinds of analytical tools such as XPS, AES, RHEED and TEM[1~3]. However, there still remains a number of important problems in silicide formation; initial growth, intermixing between metal and silicon, phase sequence and so on. Recently the growth morphology of titanium silicides formed from ultrathin titanium films on Si(100) substrate has been studied by scanning tunneling microscope(STM)[4]. Although they showed the various stages of the silicide formation, the initial nucleation and growth process still remains unclear.

In this paper, we investigated the nucleation of titanium at room temperature and the initial growth of titanium silicide at elevated temperature on Si(111)7×7 surface structures using STM in ultrahigh vacuum chamber.

2 Experiment

The experiment was carried out in UHV chambers(base pressure less than 1×10^{-10}Torr) equipped with STM, XPS, and electron gun evaporator. STM observation was performed at room temperature.

Single crystalline phosphorus-doped n-type (111) CZ Si wafers with resistivity of 0.7-1.3Ωcm were used. Sample were heated at 600°C for more than 10 hours for degassing and then cleaned by flashing at 1250°C for 10 seconds several times. After this stage, STM images of a clean Si(111)7×7 reconstructed surface structure was obtained. Ti(99.99% purity) was evaporated at room temperature using an electron gun evaporator. For the study of silicide growth, samples were annealed t 600°C and 700°C for 10 min. STM images presented here are obtained with +2V positive bias and some images are taken with -2V negative bias.

3 Results and Discussion

XPS measurements were performed to determine the chemical identification regarding the following elements; C, Ta(crucible material), Ti and Si after evaporating Ti at a coverage of 10^{-2}L. In XPS analysis, only Ti and Si signals were observed. Thus the adsorbed materials were to be Ti and the contamination of C, Ta and O were negligible.

Fig.1 shows STM image at the coverages of 10^{-3}L Ti depositions at room temperatures. A large fraction of the surface show the Si(111)7×7 reconstruction. The average diameter of clusters is estimated to be 9.4Å, containing several titanium atoms. It is noted that in STM image of Fig.1 many dark sites are observed around the bright area. Generally, dark sites in STM image result from the missing atoms or the reduction of density of state. Since Ti is known to react with Si even at room temperature, dark sites will be associated with the latter origin.

The site selectivity of Ti for Si(111)7×7 unit cell was investigated by the STM measurement with neg-

ative sample bias. STM image was shown in Fig.2 for a sample at a coverage of 10^{-3}L. Bright sites are the faulted sites and dark sites are the unfaulted sites in Si(111)7×7 surface structures. It is clearly shown that titanium atoms were preferentially adsorbed on the faulted-half of Si(111)7×7 surface. About 70% Ti prefer to locate on the faulted sites. It has been reported that in Pd adsorption on Si(111), 95% Pd locates on the faulted sites[5]. Such strong site selectivity was not observed in case of Ti. It has been reported that growth mode of Ti on Si(111)7×7 at room temperature is a Stranski-Krastanov type from the RHEED experiment[1]. As shown in the sequence of STM images at RT in Fig.1, Ti is nucleated preferentially on the faulted site of 7×7 unit cell at the initial stage of Ti deposition, and the deposited Ti atoms coalesce to form the islandlike cluster with the increase of the Ti coverage. Thus the growth mode of Ti at room temperature is not a Stranski-Krastanov mode.

Fig.3 and 4 show the STM images of the sample deposited with Ti at room temperature at 10^{-3}L coverage followed by annealing at 600°C and 700°C for 10 min, respectively. At 600°C, two different structures, island and platelike structures, are observed. After annealing, the density of island decreases, while its size increases as compared with the results at room temperature(Fig.1). Although the composite of the structure is unknown, silicide formation occurs at these temperatures. It is found from a line profile of STM that the island has a three dimensional shape. Thus they may be the amorphous titanium silicide. On the other hand, island disappears and only plate structures are observed at 700°C. This plate structure has a two dimensional shape, being the crystalline titanium silicide. The interesting feature is that the top of the plate structure is almost flat as shown from the insert of Fig.4. The height of the plate is 2~3 times of that of Si(111) 7×7 step-height(3.1Å). It is known that $TiSi_2$ has two kinds of crystalline structures: C49 and C54 type. C54-$TiSi_2$ has a structure of face-centered orthorhombic with lattice parameters of a=0.826nm, b=0.480nm and c=0.853nm. Thus the plate structure suggests the monolayer growth of C54-$TiSi_2$.

Considering STM images of Fig.3 and 4, very interesting other features are also obtained. First, titanium silicide grows directly from islandlike to platelike structures. This direct conversion from island to plate indicates the change from amorphous to crystalline phase. Such direct island to plate growth mode suggests the fundamental process of the titanium silicide thin film growth. Second, growth direction of platelike silicide is parallel to $[10\bar{1}]$ and $[01\bar{1}]$ directions. This is the rhombic side direction passing through the corner holes in Si(111)7×7 unit cells. That is, the growth direction of titanium silicide reflects the surface structure of the underlying Si substrate.

4 Conclusion

We have studied the nucleation of titanium at room temperature and the initial growth of titanium silicide at elevated temperature on Si(111)7×7 surface structures using the scanning tunneling microscope. At room temperature Ti is nucleate preferentially on the faulted halves of 7×7 unit cell, and the deposited Ti atoms coalesce to form the islandlike cluster with the increase of the Ti coverage. Its growth mode at room temperature is not Stranski-Krastanov type. Annealing after the room temperature Ti deposition drives the growth of plate structures from island structures, corresponding to the change from amorphous to crystalline titanium silicide. Direct island to plate growth mode suggests the fundamental process of the silicide thin film growth. The plate structure's top is flat and their height is 2~3 times of that of step-height Si(111) surface. The growth direction of platelike titanium silicide is reflected by the underlying Si surface structure.

Reference

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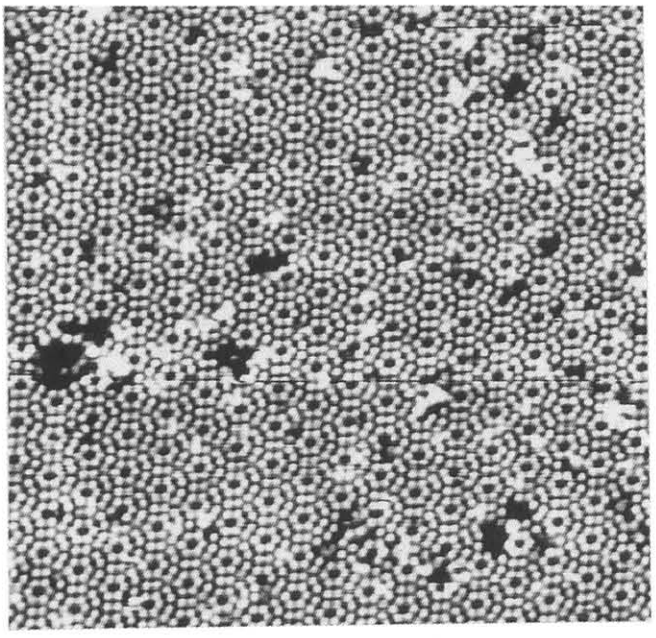

Fig.1: STM image of Ti adsorbed Si(111)7×7 surface at room temperature.
(sample bias +2V)

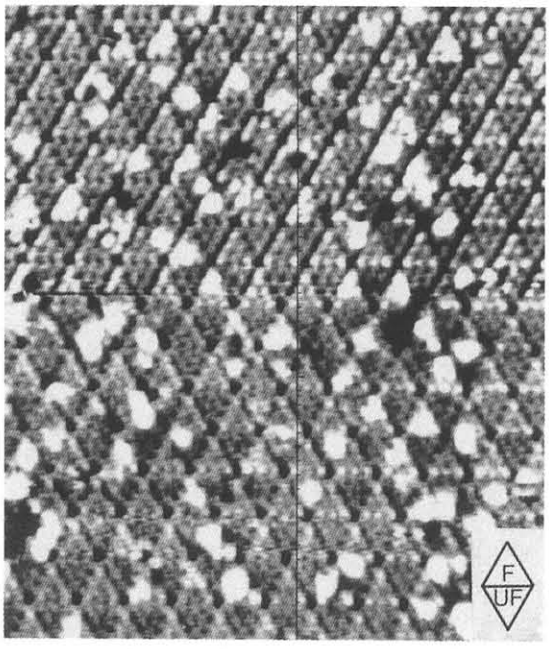

Fig.2: STM image of Ti adsorbed Si(111)7×7 surface at room temperature.
(sample bias -2V)

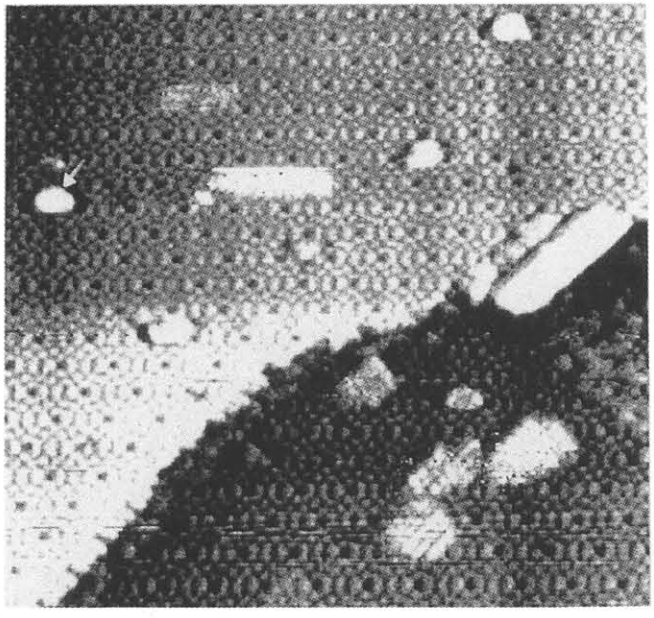

Fig.3: STM image of Ti adsorbed Si(111)7×7 surface after 600°C annealing.
(sample bias +2V)

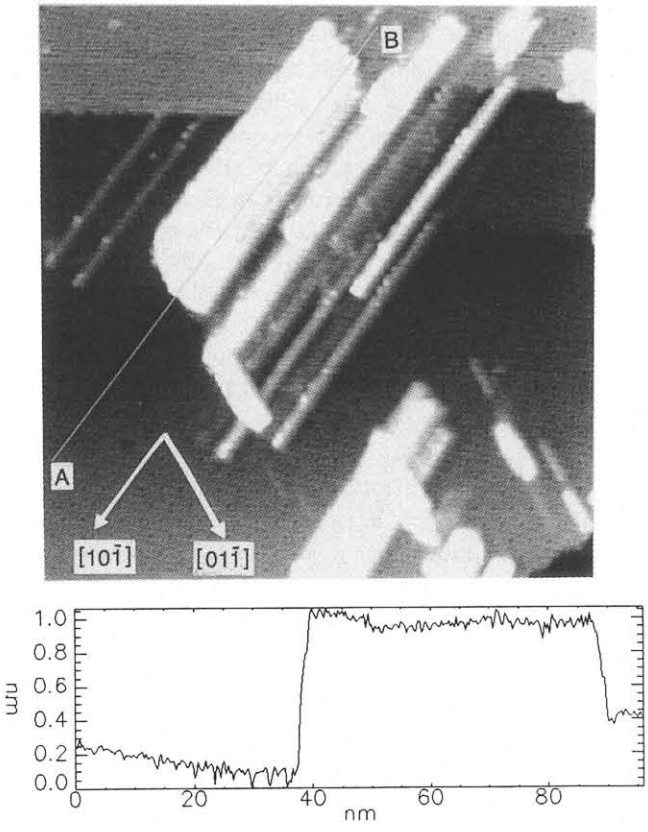

Fig.4: STM image of Ti adsorbed Si(111)7×7 surface after 700°C annealing.
(sample bias +2V)