REAL-TIME OBSERVATION OF TI SILICIDE EPITAXIAL ISLANDS GROWTH WITH THE PHOTOELECTRON EMISSION MICROSCOPY

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ABSTRACT

The formation of nanoscale Ti silicide islands was observed by Photo-electron emission microscopy (PEEM). The islands were prepared by deposition of an ultrathin Ti (3-12ML) on Si(001) at room temperature and at an elevated temperature of 950°C. The island formation was initiated by *in situ* annealing to 1150°C. It was observed that initially Ti silicide islands form while longer annealing indicates some islands move and coalesce with other islands. Most of the islands are similar in size and have relatively uniform separation. Also, it was shown that for continued Ti deposition at a temperature of 950°C, the density of islands did not increase. However, islands grew together when their perimeter lines touch each other. The results are described in terms of island growth processes of coalescence and ripening.

INTRODUCTION

Photo-electron emission microscopy (PEEM) is an emission microscopy technique in which images of a solid surface are formed by photo excited electrons. Typically, ultra violet (UV) light above the photoelectron threshold will cause electrons to be emitted from a surface. The photo excited electrons originate from the near surface region (~10nm), and essentially reflect the electronic structure of the surface. These electrons may be accelerated and imaged, and the image will reflect the properties of the surface. PEEM has already been used to investigate surface chemistry of metals [1], epitaxial growth of materials [2] and characterization of semiconductor devices [3]. PEEM allows real time observation and direct imaging during processing with monolayer surface sensitivity and high resolution (~10nm). For this reason, PEEM is particularly suited for measurement of dynamical processes on semiconductor surfaces.

In this study, PEEM is used to obtain the growth of nanoscale epitaxial silicide islands on Si surface. The image contrast mechanism for a metal on a semiconductor system is the energy difference between the work function (WF) of a metal and the photo-threshold of the semiconductor (The semiconductor photo-threshold is the energy to excite an electron from the valence band to the vacuum level). Therefore, $TiSi_2$ islands on a Si surface would be imaged by this contrast mechanism. The photon energy of the employed UV-light should be below the photo-threshold of silicon and above the WF of the Ti silicide. In this case, electrons will be emitted from regions with Ti and no emission will occur from exposed Si surfaces.

Our previous studies have shown the tendency of $TiSi_2$ on Si to form epitaxial island structures. Furthermore, for ultrathin Ti (<1nm) deposited on Si substrate followed by high temperature annealing (~1000°C), similarly sized islands of Ti silicide (~30nm) were obtained to be uniformly distributed over the Si (001) surface [4-6]. The Ti silicide island size and spatial distribution were very dependent on the growth conditions (i.e. Ti layer thickness, annealing temperature and surface roughness)[4,5]. It was suggested that the narrow island distribution is due to surface diffusion and the strain field effect induced in the substrate by the islands.

In this study, the formation of Ti silicide islands is explored with thin Ti deposition of 3-12 monolayers(ML) on Si(001) substrates. During in situ annealing at temperatures up to 1150°C, the island formation process and dynamics are observed in real-time with PEEM. After Ti silicide island formation, the surfaces are *ex-situ* analyzed with AFM and SEM to compare the surface morphology with the results from the PEEM. The size and distribution of islands are

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obtained, and the island growth is explained in terms of coalescence and ripening growth processes.

EXPERIMENT

The experiments were performed in an UHV PEEM system obtained from Elmitech. This system allowed heating of the substrates to > 1200°C, and the chamber is equipped with a Ti-filament deposition source. The base pressure in this system was < 2 x 10^{-10} Torr. The electric potential used for accelerating the imaging electrons is approximately 20kV across a gap of 2mm. The UV-light source is a Hg discharge lamp with upper cut-off energy near 5.1eV. We have demonstrated the resolution of our system to be ~12nm using a 100W Hg lamp as the UV excitation.

Sections of silicon (001) wafers (n-type, P-doped, resistivity 0.8-1.2 Ω-cm, 9x9mm^2) were used as substrates. The wafers were cleaned first by uv-ozone exposure and then by an HF based spin etch (HF:H_2O:ethanal=1:1:10). After *ex-situ* cleaning, the wafers were mounted to the sample holder and then introduced into the PEEM chamber. Before Ti deposition, the wafer was heated at a temperature of 800°C for 10 minutes by filament radiation and electron bombardment from the backside in a sample holder. The residual oxide and hydrogen were removed by the heat treatment. After cleaning, RHEED displayed a 2x1 pattern typical of the Si(001) reconstructed surface. Titanium was deposited *in situ* from the hot-filament titanium source in the PEEM chamber onto the cleaned sample which was held at room temperature or a temperature of 950°C. The titanium layer thickness was 3-12 monolayers (ML) with a deposition rate of 1ML/20S. To observe the Ti silicide island formation process, the substrates were annealed in UHV from 100°C up to 1200°C in 100°C increments for intervals of 10 minutes.

The PEEM images were displayed with a microchannel plate and phosphor screen installed in the PEEM which was monitored with a CCD camera. The images were simultaneously stored digitally with an image processor and on video tape. Image acquisition was obtained with a real-time image processor (DSP-2000) which is capable of integration of up to 128 single frames. For the data presented here, sixteen successive images were integrated. The resulting images correspond to a signal integrated over 16/30th of a second. After the substrates were unloaded from the PEEM, *ex-situ* AFM and SEM were performed to compare the surface morphology.

RESULTS

Initially, we monitored the surface morphology and the Ti silicide island formation processes while titanium is deposited on a clean Si(001) substrate followed by annealing to 1150°C. The PEEM images showed the overall surface of the Si as bright for the as-loaded wafers which became uniformly dark after the heat cleaning. The results suggest that the photo-threshold of the oxide terminated and the cleaned surfaces are below and above cut-off energy of Hg lamp(5.1eV), respectively. After Ti deposition of 10ML on the clean surface, the image is uniformly bright as the whole surface was covered uniformly by titanium (the WF of Ti is ~4.4eV). During annealing up to 700°C, the images of the surface did not change but grew darker. The darker surface indicates that the Si from the substrate has diffused into the overlayer of Ti, and a Ti silicide phase has formed. Our previous study showed Ti silicide island formation at this temperature [6]. One possibility to explain these inconsistent results may be that the photoelectron yield is too low to image the small islands. However, as shown in Fig. 1 separated $TiSi_2$ islands were observed after annealing at 1000°C. The image contrast originates from the photo-threshold difference between $TiSi_2$ (~4.6eV) and Si (>5.1eV).

Fig. 1 shows a sequential PEEM image of the $TiSi_2$ island formation sequence as the substrate is held at 1150°C for 15 minutes. Initially, similar sized islands are distributed uniformly and completely separated (Fig. 1-a). As the annealing time increases, the average size of the islands increases gradually, and the number of islands decreases (Fig. 1-f). Fig. 2 shows that the number of islands decreases for longer annealing time. The data is fitted with an

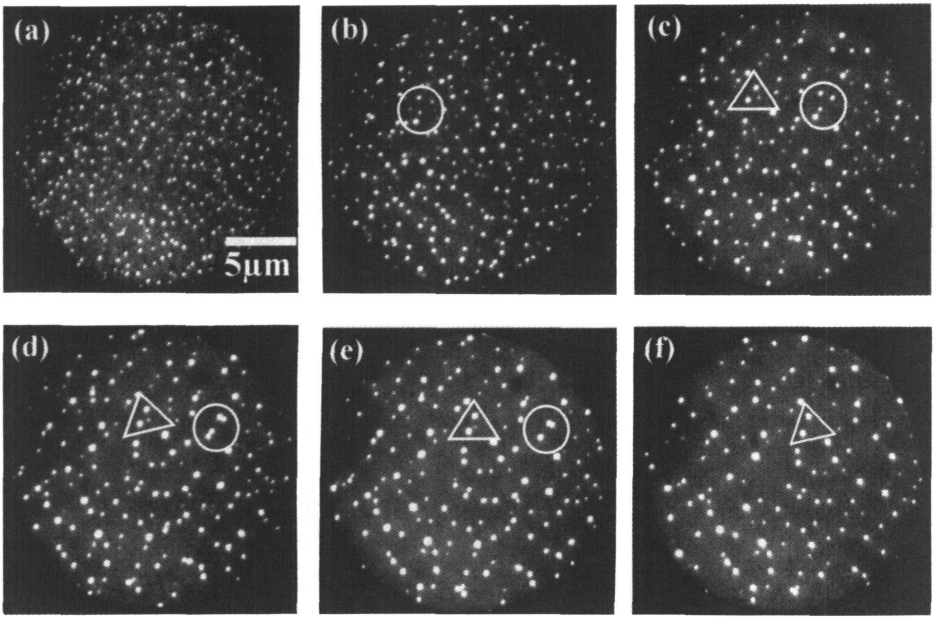

Fig. 1 PEEM images of 10ML Ti deposition followed by annealing at 1150°C for (a) 1min (b) 5min (c) 9 min (d) 10min (e) 11min (f) 15min. The islands (in the circle) coalesce and grow larger. The field of view of each image is 20μm. All images were obtained in situ, real time with the sample at the annealing temperature. The image shift is due to specimen drift at the elevated temperature.

exponential. Examination of islands highlighted by the circles in Fig. 1(b)-(e) indicates a coalescence growth process. The islands, with substantial thermal energy, diffuse on the surface. In this sequence, close islands are observed to combine with each other and transform into larger islands. The triangles in Fig. 1(c)-(f) display another island growth process. The large islands grow larger while the small islands disappear. This is characteristic of ripening integrated by surface diffusion.

Ex-situ AFM measurements of the same sample also display a uniform lateral and vertical size of the islands (Fig. 3). The average lateral size of the islands is ~500nm and the height is ~200nm. In comparison with our previous study (diameter of island: 50nm, height: 5nm) [4], the islands are larger and are separated by greater distances. This difference is attributed to different growth conditions (increased Ti thickness and higher annealing temperature). The SEM measurements also show a similar island distribution. The shape of the islands could be observed by tilting the sample be 60°[Fig. 4]. The larger islands are observed to be flatter than smaller ones. An interesting aspect of the shape of islands is the bump of Si under each island [Fig. 4-a]. This shape may be influenced by the high electric field of $\sim 10^7$ V/m between the sample and cathode lens of the PEEM.

To monitor the island formation during deposition at an elevated temperature, 3-12ML of Ti was deposited continuously at a temperature of 950°C (Fig. 5). It was observed that the growth mode of the Ti silicide at the high temperature is 3d-island growth (Volmer-Weber mode). Also, more dense and smaller islands were formed compared with Ti deposition followed by annealing at the same temperature. The density and average size of the islands did

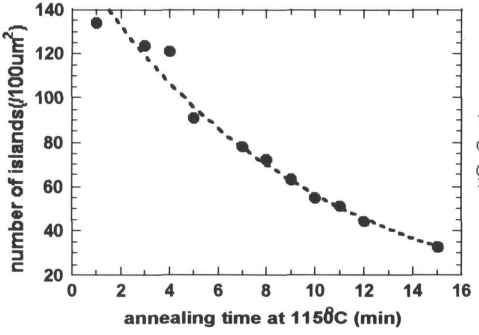

Fig. 2 The number density of islands observed at 1150°C as a function of annealing time.

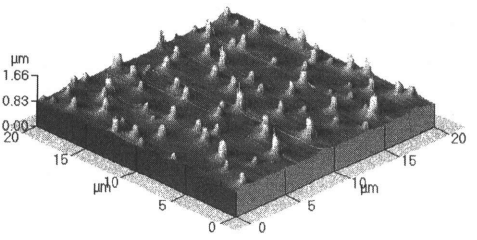

Fig. 3 A 20 x 20 μm^2 AFM 3D-rending image of 10ML Ti deposition annealed at 1150°C.

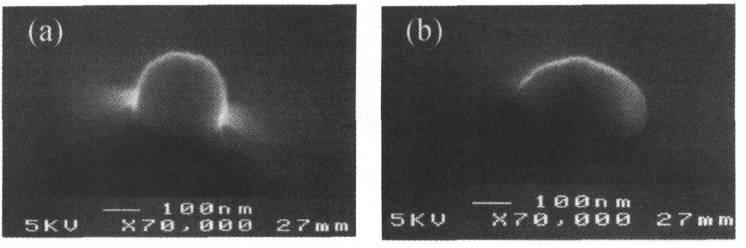

Fig. 4 SEM micrographs of $TiSi_2$ islands showing the different shape and size of island. The sample was tilted 60° with respect to horizon.

not increase even though the Ti thickness increased. However, islands next to each other coalesced as the deposition thickness of Ti increases. In order to observe the motion and coalescence of these islands, it would be necessary to obtain images with higher magnification. Unfortunately, the low intensity of the electron emission from these samples limited the magnification of the PEEM.

We observed another image contrast mechanism with the sample at high temperature. During annealing at ~1100°C, the image of the Ti silicide islands could be obtained without the UV-light. Furthermore, the overall brightness of the image was enhanced with increasing temperature (compare Fig. 1 with Fig. 5). A sample heated to a sufficient temperature will emit thermionic electrons. These electrons will also be imaged in the PEEM. Thus, strictly speaking. PEEM over a range of temperatures utilizes the processes of both photoemission and thermionic electron emission.

DISCUSSION

Consider the growth processes of Ti silicide islands at high temperature (Fig. 1). Previous studies have explained the island formation in terms of the surface and interface energies of the structures [4-6]. Here we suggest two possibilities to account for the increasing size of the islands and the decreasing density obtained at the higher temperature annealing. One growth

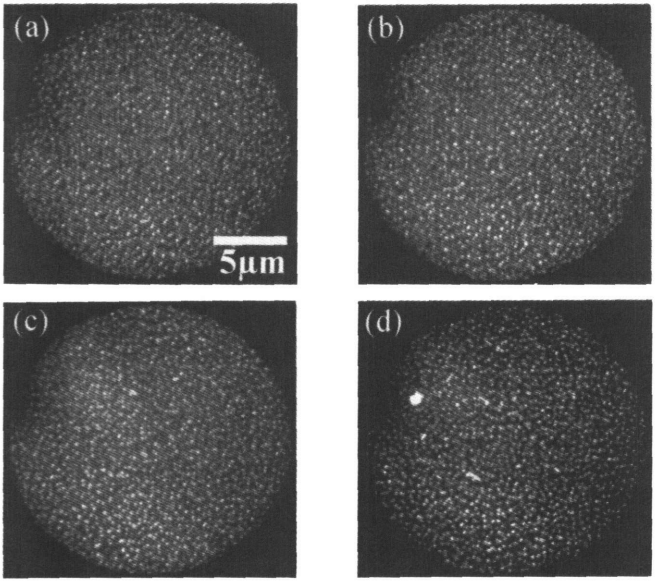

Fig. 5 PEEM images of Ti silicide islands formed with continuous deposition at 950°C. Ti deposition thickness is 3, 6, 9, 12ML for (a) through (d), respectively. All images were obtained after cooling down to room temperature. The field of view of each image is 20μm.

process is island coalescence (the circle in Fig. 1 (b)-(e)). After the islands are grown epitaxially (facetted islands) by annealing at high temperature, substantial thermal energy could allow the islands to diffuse on the surface. Finally, the islands grow together upon when they come into close proximity. The other growth process is island ripening (the triangle in Fig. 1 (c)-(f)). It is characterized by a local interaction between two neighboring islands of slightly different size. Thermodynamically each island grows and disintegrates with the same probability. Due to the difference in island circumference, the larger islands grow at the expense of smaller islands. Both growth processes may reduce the surface-to-volume ratio of the employed system and result in a minimization of the total surface energy.

For the case of continuous deposition of Ti at high temperature (Fig. 5), we observed another mechanism of island formation. At the earliest stages, Ti silicide island initiation is a spatially random process. The spatial distance between the islands is too far to interact by the island-induced strain fields. Further deposition results in strain field overlapping caused by the dense and large islands. The adatoms on surface between the islands are preferentially adsorbed by larger islands. Furthermore, at the late stages, continued deposition allows the islands to grow together. This is another coalescence mechanism of island growth. The islands remain relatively in place because of the lower temperature. However, with continuing deposition these islands grow larger at the perimeter of the islands. The islands coalesce when their perimeter lines touch each other and grow together. This process of coalescence can be referred to as static coalescence, compared with the dynamic coalescence process of the high temperature annealed samples [7].

Small islands (~30nm diameter) were not observed, even though our PEEM instrument has a high resolution capability of ~10nm. Regardless of the aberration of lens, the image resolution is limited by the emission current density. The emission current density depends upon the quantum efficiency (emitted electrons per incident photons) of the surface and the photon flux density of light source. We can estimate the photon flux and the current density required for imaging an island of ~ 10nm. A current density of > 1.6×10^{-4} A/cm^2 is required to observe the islands of ~10nm. Given a quantum efficiency of ~ 10^{-6} range as an average of many materials (pure metal : > 10^{-5}), the desired photon flux could be ~10^{21} photons/sec·cm^2. The photon flux of the Hg discharge lamp is several orders of magnitude lower than this(~10^{14} photons/ sec·cm^2). Therefore, a higher intensity UV source will improve the imaging of smaller islands. Secondarily, chromatic aberration, which is caused from a spread in the velocity of the emission electron, blurs the image resolution. If a photon source with a small energy spread would be tuned to just above the work function of Ti silicide (~4.6eV), better image contrast of the Ti silicide islands should be achieved. If we can use an intense tunable light source with a narrow energy distribution, we may observe small Ti silicide island formation and dynamics. In the future, as we combine our PEEM with the UV-FEL at Duke University for a light source (the photon flux: >10^{25}/sec·cm^2, energy range: 3-10eV, energy resolution: $\Delta E/E > 10^{-4}$), we anticipate real time imaging of surface Dynamics at the 10nm resolution limit of the PEEM.

CONCLUSION

In this study, we have used PEEM to observe the formation and real-time dynamics of Ti silicide islands on Si (001). Similar sized and relatively uniformly separated islands were observed for Ti deposition followed by annealing or Ti deposition at high temperature. Both growth processes of coalescence and ripening contribute to large island growth for high temperature annealing. For continuous deposition of Ti, the island growth process is characterized as static coalescence. In the future, PEEM combined with a high intensity and tunable UV-FEL should promise observation of small island formation (~10nm) and real time surface dynamics.

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