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Shape transition in the epitaxial growth of gold silicide in Au thin films on Si(111)

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Growth of epitaxial gold silicide islands has been observed when an Au film deposited on a bromine-passivated vicinal (4° misoriented) Si(111) substrate was annealed around the Au-Si eutectic temperature. The islands grow in the shape of equilateral triangles, reflecting the symmetry of the (111) substrate, up to a critical size beyond which the symmetry of the structure is broken, resulting in a shape transition from triangle to trapezoid. The island edges are aligned along the three equivalent $\{1\bar{1}0\}$ directions of the Si(111) surface. The elongated islands, instead of growing along three equivalent $\{1\bar{1}0\}$ directions, grow only along one preferential direction. This has been attributed to the vicinality of the substrate surface as the steps on this substrate are expected to run along the observed preferential growth direction. We have observed, under various conditions, elongated islands with an aspect ratio as large as 15:1.

I. INTRODUCTION

Heteroepitaxy produces strained epitaxial layers due to lattice mismatch between the substrate and the overlayer. Strained epitaxial layers have interesting properties and are important in semiconductor devices.[1] Since these layers are inherently unstable it is important to understand the mechanism of relaxation of strain. It has been known for a long time that the formation of dislocations is a strain relief mechanism.[2,3] However, in recent years it has been recognized that strained layers are unstable against shape changes.[4–7] Thus shape changes, such as island formation, have been identified as a major mechanism for strain relief. Recently Tersoff and Tromp[7] have given an analytical theory and shown that strained epitaxial islands, as they grow in size, may undergo a shape transition. Below a critical size, islands have a compact symmetric shape. However, at larger sizes, they adopt a long thin shape, which allows better elastic relaxation of the island stress. They observed such elongated island growth of Ag on a Si(001) surface. Prior to this, various other groups also observed elongated island growth of Ge on Si(001),[8] Au on Ag(110),[9] Au on Mo(111), and on Si(111),[10] GaAs on Si,[11] and gold silicide on Si(111).[10] In all the aforementioned cases where elongated island growth was observed, the deposition was performed under ultrahigh vacuum (UHV) condition in the submonolayer to few-monolayer range and on atomically clean substrates, and none of them provides data concerning the shape transition.

Here we present our observation of the growth of large epitaxial gold silicide islands on Si(111) substrates in a non-UHV method, and their shape transition. Our method uses a chemically Br-passivated Si(111) substrate, high vacuum evaporation of a Au film onto it, and high vacuum annealing to form a gold silicide.

The choice of the Br-passivated Si(111) substrate is based on previous studies of Br chemisorption on Si(111) substrates, and the interdiffusion behavior across the interface of a Cu film and a Br-passivated Si(111) substrate. Adsorption of bromine on silicon surfaces has been studied extensively. In most of these studies bromine chemisorption was attained from a weak bromine-methanol solution.[12–16] This non-UHV method of Br-adsorption yielded almost identical results regarding the Br-adsorption site and Si-Br bond length compared to UHV studies.[17] These results are also in good agreement with theoretical calculations.[18] Considering that the chemically prepared Br-adsorbed silicon surfaces have other expected impurities such as O and C,[19] it is striking that agreement with the UHV results exists as far as Br adsorption is concerned. It has also been shown that the Br-adsorbed Si(111) surface is extremely stable in open air.[13,15,16] Br adsorption in this case inhibits substrate surface oxidation. For the growth of a silicide from a metal film on a silicon substrate, it is important that diffusion across the interface is not hindered. The presence of an oxide layer at the interface is known to hinder the diffusion across the interface.[20–22] It is also known that the diffusion behavior is comparable in cases where a metal film is deposited on a chemically prepared Br-passivated Si(111) substrate or an atomically clean Si(111) (7×7)-reconstructed substrate.[21,22]

The passivity of the Br-adsorbed Si(111) surface has some similarity to the As-passivated Si(111) surface. While for the Br-passivated surface the surface Si dangling bond is saturated, for the As-passivated surface the Si dangling bond is replaced by a passive electron lone pair.[23] The study of epitaxial growth on Br-passivated substrates is also interesting in light of recent activities on the surfactant-mediated epitaxial growth.[24] As and other impurities on silicon surfaces have been used for this purpose.[24,25] Br passivation of the Si(111) surface, like As passivation, reduces the substrate surface free energy.

We will discuss the shape transition in the epitaxial gold silicide islands in the light of the Tersoff and Tromp theory.[7] This theory, although developed for a coherent epitaxial system, allows for a description of partially coherent systems. The large critical size of the silicide islands observed in our study will be discussed in terms of partially coherent epitaxial structures.

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II. EXPERIMENT

We used a non-UHV method to obtain the gold silicide island structures on silicon substrates. The method involves gold evaporation onto a bromine-passivated Si(111) polished wafer (n-type, Sb-doped, 0.005–0.02 Ω cm) substrate and subsequent annealing. The details of the substrate preparation have been discussed elsewhere.[21,22] The method used for the bromine passivation of the Si(111) surface is known to provide Br adsorption ($\approx\frac{1}{4}$ monolayer) at the atop site on the surface Si dangling bonds on hydrofloric acid-etched[13] or cleaved[16] Si(111) surfaces. [One monolayer (ML) on a Si(111) surface is equivalent to 7.84×10^{14} atoms/cm^2.] Br adsorption inhibits the surface oxidation process. A detailed x-ray photoelectron spectroscopic characterization of Br-treated Si surfaces has been published elsewhere.[19]

In the present work a 120-nm thin Au film was evaporated from a W basket onto a Br-passivated Si(111) substrate at room temperature in high vacuum (3×10^{-4} Pa). Then the samples was annealed at 360 °C; that is, around the Au-Si eutectic temperature (363 °C), for 20 min in high vacuum. This gave rise to triangular and trapezoidal gold silicide island structures. Different features on the annealed surface were studied by Rutherford backscattering spectrometry (RBS), optical microscopy, scanning electron microscopy (SEM), and energy dispersive x-ray (EDX) analysis.

III. RESULTS AND DISCUSSIONS

A. General aspects

1. Characteristics of as-deposited and annealed films

RBS measurements were made on as-deposited samples, i.e., on the Au film deposited on a Br-adsorbed Si(111) surface as well as on annealed samples. These measurements were made using a 2-MeV He$^+$ beam from the 3-MV tandem van de Graaff accelerator in our laboratory. This experimental setup has been described elsewhere.[22] The spectrum for the as-deposited sample (not shown here) indicates that the Au film is laterally uniform. The thickness of the film has been determined from the RBS spectrum. From the RBS spectra of the annealed sample it was evident that the film had become nonuniform upon annealing. We observed the sample under an optical microscope and found various features. Two optical micrographs of the annealed sample are shown in Figs. 1 and 2, which reveal islands of equilateral triangular and trapezoidal shapes. As seen in the color micrographs (not shown here) the triangular and trapezoidal islands and the flat background regions have gray color, while the stringy structures are golden. Lateral nonuniformity of the film is obvious from Figs. 1 and 2. One may ask why different features are observed on different regions of the substrate. One possible answer may lie in the nonuniformity of the substrate surface passivation by Br. It is known that on a well-oriented[13] or stepped (vicinal) (Ref. 16) surface the chemical preparation provides only $<\frac{1}{3}$ ML of covalently bonded Br at the atop site on the Si(111) surface. The rest ($\gtrsim\frac{2}{3}$ ML) of surface Si atoms are bonded with oxygen or other impurities, as observed in the x-ray photoemission spectroscopy (XPS) studies.[19] There is some residual oxide just after the preparation of the Br-passivated substrate. It is known that for a Au film evaporated on Si(111) surfaces, Si diffuses rapidly through the evaporated film to form a silicide, provided that it can enter the Au layer through the interface. This entrance into the overlayer is hindered when the Si surface is covered with an oxide layer.[26] We have also shown this diffusion hindering behavior of oxide for Cu films on Si(111) surfaces.[21,22] Also for the Au-Si system, when the Si substrate has a native oxide layer, even annealing at 600 °C for 20 min does not show the formation of silicide. At 300 °C the self-diffusion coefficient of Au and the Au/Si interdiffusion

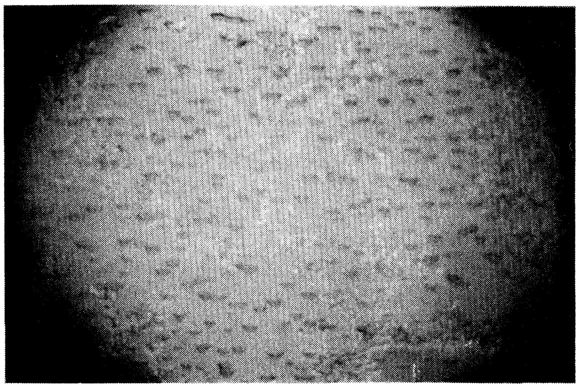

FIG. 1. Photomicrograph showing Au$_4$Si islands, that is, epitaxial Au$_4$Si crystallites on the Si(111) substrate. The threefold symmetry is reflected in the shape of many islands. Smaller structures are formed for shorter duration of annealing. The diameter of the image is 400 μm.

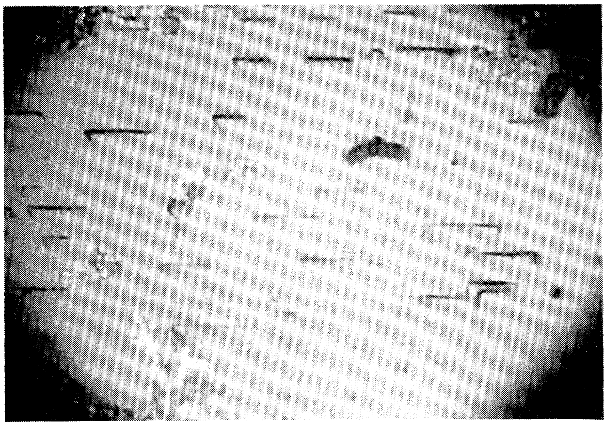

FIG. 2. Au$_4$Si islands in the shape of a trapezoid. Although the islands vary in length, their width remains practically constant and approximately equal that of the largest triangular islands. The diameter of the image is 400 μm.

coefficient are comparable. Thus in the Br-passivated region, considerable diffusion across the interface will allow nucleation and growth of gold silicide, and in the oxide-covered region lateral diffusion of Au would be more likely. Later diffusion of Au toward the silicide islands and outdiffusion of Si in the island region would help the island grow leaving Au-depleted regions around. In the region where fewer nucleation centers are available, Au would tend to agglomerate. In the RBS spectra for the annealed sample a tiny peak at the highest energy can be attributed to a thin uniform layer (~5 nm) containing Au besides the island structures. Details of the general aspects appear elsewhere.[27]

2. *Compositions of the various observed structures*

In the EDX analysis we used electron beams of energies 10 and 25 keV to probe different depths. The lateral extension of the probe beam was ~1 μm. The incident e^- beam caused ionization of the elements present in the volume leading to x-ray emission from the constituent elements. The x rays were detected with a Si(Li) detector. The composition was obtained from the analysis of the relative intensities of x rays. For 10-keV incident electrons Au-*M* and Si-*K* fluorescence photons were detected. For the 25-keV incident electrons Au-*L* and Si-*K* were detected. The average composition of the triangular and trapezoidal islands obtained with 10-keV electrons are $(79\pm3)\%$ Au and $(21\pm3)\%$ Si (averaged over nine islands) and with 25-keV electrons $(78\pm5)\%$ Au and $(22\pm5)\%$ Si (averaged over six islands, different sample). This composition is close to the eutectic composition.[28] We write this composition to be Au_4Si. Green and Bauer[26] studied Au deposition on an atomically clean Si(111) (7×7)-reconstructed surface under UHV conditions. They also observed the formation of gold silicide (83% Au, 17% Si) when a thin Au film on Si(111) was annealed.

From the EDX analysis the heights of our observed islands are estimated to be $\gtrsim 1$ μm. We have measured the island thickness for gold silicide islands on another sample with comparable initial Au thickness by secondary-ion-mass spectrometry (SIMS). These islands show a constant thickness of 1.23 μm and an abrupt silicide/silicon interface.

The composition obtained from EDX analysis of the thin flat region (Fig. 2) is not the real composition of this layer. As the probed thickness is ~1 μm and the Au-containing layer is ~5 nm, the Si content is heavily overestimated because of a large Si-$K\alpha$ contribution from the Si substrate under the layer. The similarity of color between the silicide islands and the flat regions, as observed in a color micrograph, indicates that the flat region is also gold silicide. The stringy (fractal) branches are ~100% Au. Fractal structures are more prominent in the region where silicide islands are smaller.

3. *Characteristics of the gold silicide islands*

From the optical micrograph we have observed that small silicide islands have equilateral triangular shape. This reflects the threefold symmetry of the Si(111) surface. The edges of the islands are aligned along $[1\bar{1}0]$, $[01\bar{1}]$, and $[\bar{1}01]$ directions on the Si(111) surface. The large islands are trapezoidal and, thus, the threefold symmetry is broken although the edge alignments are the same as that for the triangular islands. The trapezoidal islands observed in the optical micrographs actually show rounded corners in higher resolution as seen in the SEM micrographs, one of which is shown in Fig. 4. Long islands with rounded corners look rod shaped.[27] Gold silicide islands of similar shapes have been observed by Mundschau *et al.*[10] in their low-energy electron microscopy (LEEM) studies of gold film on an atomically clean Si(111) surface, deposited and annealed under UHV conditions. They have reported that these rod-shaped islands have a (5×1) low-energy electron-diffraction (LEED) pattern. They also observed triangular silicide islands for low Au coverages.

The trapezoidal (or rod-shaped) islands in our study are aligned along the same direction, i.e., along one of the three equivalent $\{1\bar{1}0\}$ directions. From the symmetry of the Si(111) substrate one expects them to grow along all the three equivalent directions. We attribute this symmetry breaking to the vicinality of the substrate Si(111) surface used in our study. Our substrate surface was misoriented by $(4.0\pm0.5)^\circ$ toward the $[\bar{1}\bar{1}2]$ azimuthal direction. Surface steps, which run along the $[1\bar{1}0]$ direction, are formed on this vicinal surface.[29] The trapezoidal islands observed in our study are also aligned along the $[1\bar{1}0]$ direction with the shorter edge of the parallel sides toward the $[\bar{1}\bar{1}2]$ direction. It is well known that nucleation and growth are predominant at the surface defects. Apparently growth along the steps is preferred.[29] The silicon wafer used in the study of Mundschau *et al.* was oriented within 0.4° of the (111) plane, and they observed that the rod-shaped islands are oriented along the three equivalent $\{1\bar{1}0\}$ directions as expected from the symmetry. Under various growth conditions, for silicide islands of uniform width, we observed an aspect ratio as large as ~15:1. An aspect ratio up to ~30:1 has been observed for islands of slightly nonuniform width.[27]

B. Shape transition

In Fig. 1, we notice the formation of the equilateral triangular gold silicide structures reflecting the threefold symmetry of the Si(111) surface. In Fig. 2, we observe some equilateral triangular islands which have grown larger, but mostly we notice islands of trapezoidal shape with larger areas than that of the triangular ones. The widths of all the trapezoidal islands are comparable, and are roughly equal to the width of the largest equilateral triangular islands. That is, the growth of the islands beyond a critical size, represented by the largest triangular island, is associated with the shape transition: equilateral triangle to trapezoid.

We will discuss our results in the light of the recent theory given by Tersoff and Tromp,[7] who treated the case of Ge growth on Si(100) as a generic case. For a strained island on a substrate they computed the energy of an island as a sum of two contributions—one from the relevant surface and interface energies and the other from elastic relaxation. The surface energies are those of the substrate and of the island top and edge facets, and the interface energy is that for the island-substrate interface. The second contribution arises from the fact that an island under stress exerts a force on the substrate surface, which elastically distorts the substrate. This lowers the energy of the island at the cost of some strain in the substrate. Tersoff and Tromp derived an expression for the energy per unit volume (E/V) of a rectangular strained epitaxial island:

$$\frac{E}{V}=2\Gamma(s^{-1}+t^{-1}) -2ch\left\{s^{-1}\ln\left[\frac{s}{\phi h}\right]+t^{-1}\ln\left[\frac{t}{\phi h}\right]\right\}, \qquad (1)$$

where s, t, and h are the width, length, and height of the island, respectively; $\phi=e^{-3/2}\cot\theta$, θ being the contact angle; Γ contains the surface and interface energies; and c involves the bulk stress in the island and the Poisson ratio and shear modulus of the substrate. It is clear from Eq. (1) that the surface-energy-dependent term prefers to have a large area island for stability. On the other hand the strain relaxation energy term prefers to have islands of smaller area for greater stability. The optimal tradeoff between surface energy and strain is obtained through the minimization of E/V with respect to s and t. This gives $s=t=\alpha_0$, where

$$\alpha_0=e\phi h e^{\Gamma/ch}\ . \qquad (2)$$

For island sizes $s, t<e\alpha_0$, the square island shape ($s=t$) is stable. Once the island grows beyond its optimal diameter α_0 by a factor of e, the square shape becomes unstable and a transition to rectangular shape takes place. As the island grows, the aspect ratio t/s becomes ever larger.

The above-mentioned treatment was for epitaxial islands on a Si(100) surface which has a fourfold symmetry. In this case the island growth up to the critical size has a fourfold symmetry (square). Beyond the critical size the islands grow in rectangular shape. These rectangular islands have been called self-assembling quasi-one-dimensional quantum wires. In our case the substrate, Si(111), has a threefold symmetry. Therefore, the islands up to the critical size are of equilateral triangular shape and the shape transition is from triangle to trapezoid. Here in the initial stage of the growth the triangular islands are of submicrometer size. With higher resolution microscopy, at the early stage of growth, one can possibly identify islands of much smaller sizes. These islands may be called self-assembling quasi-zero-dimensional quantum dots. The trapezoidal islands, as seen in Fig. 2, are not very long. However, they can grow longer under appropriate conditions.[27]

At this point let us try to make some quantitative estimates from the triangular and trapezoidal islands observed in our experiments. Figure 3(b) shows the plots of l_1 and l_2 versus island area A. It is seen that the islands grow as equilateral triangles ($l_1=l_2=l_0$) up to a critical size beyond which there is a transition to trapezoid ($l_2>l_1$). For the largest triangular islands the area is $\sqrt{3}l_0^2/4=110\ \mu\text{m}^2$ (measured). In the light of Tersoff and Tromp theory, we attempt to give an approximate estimation of the energy per unit volume (E/V). We set the area of the island, where the shape transition takes place, $e^2\alpha_0^2=110\ \mu\text{m}^2$. This provides $\alpha_0=3.86\ \mu\text{m}$. Assuming $h=1\ \mu\text{m}$ and $\theta=45°$, we get $\Gamma/ch=1.85$. For the trapezoidal islands we use $s=\sqrt{3}l_1/2$ and $t=l_2-s/\sqrt{3}$ ($A=st$) and use Eq. (1) to evaluate E/V. For the triangular islands we use $s=\sqrt{3}l_1/2$ and $t=l_2/2$ ($A=st$) to evaluate E/V. The results are shown in Fig. 3(a).[30] Our results are in reasonable agreement with the gross features of the Tersoff and Tromp theory. However, we do not observe the sharp change in the aspect ratio around the transition point as predicted by the theory. If the second derivative of the energy with respect to the island size is discontinuous, as mentioned in Ref. 7, its magnitude must be too small to be detected in the present experiment.

The detailed features of the gold silicide islands are not visible in the optical micrographs shown in Figs. 1 and 2. A scanning electron micrograph is shown in Fig. 4. The patterns with pin-hole structures on the islands indicate

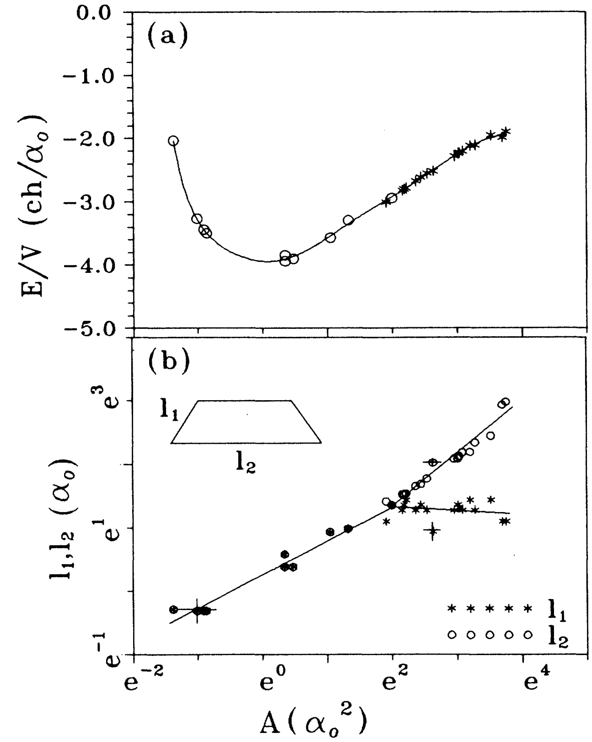

FIG. 3. (a) Computed energy per unit volume of island, in units of ch/α_0, vs measured island area A (○, triangle, ∗, trapezoid). The solid line is a polynomial fit. Beyond the transition point, if the islands remained triangular the energy would be slightly (only 7% for the largest island) higher. (b) Lengths l_1 and l_2 (as shown in the inset) of the islands vs A. The unit of length for l_1 and l_2 is α_0 and that of A is α_0^2 [see text and Eq. (2)]. Solid lines are to guide the eye. For $A<e^2\alpha_0^2$, l_1 and l_2 are equal (equilateral triangle).

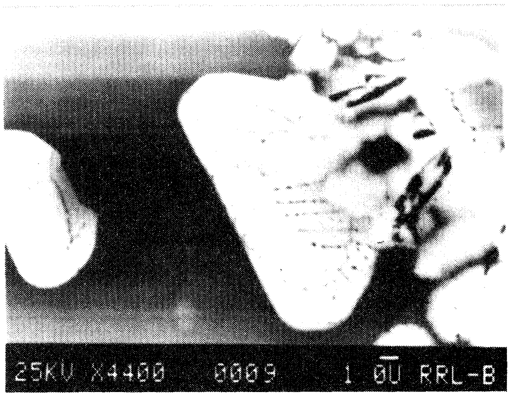

FIG. 4. A scanning electron micrograph showing pin-hole patterns in the strained Au_4Si islands. The length of the middle island is $\approx 20\ \mu m$.

the presence of dislocations. In fact, in some cases we observed a porous structure for the islands. Thus, in addition to the mechanism of shape transition for strain relief, there is a partial strain relief through the formation of dislocations in these strained epitaxial silicide islands. As Tersoff and Tromp[7] point out, a partial strain relief through dislocations would not affect the general aspects of the shape transition except for reducing the effective value of bulk stress of the island material. The parameter c in Eqs. (1) and (2) is proportional to σ_b^2, where σ_b is the bulk stress component of the island material parallel to the interface. When the presence of dislocations in the island reduces the effective value of σ_b, we see from Eq. (2) that the critical size (α_0) increases. This might be partly responsible for the large size (area about four orders of magnitude as large as that observed in Ref. 10 for the same aspect ratio) of the gold silicide islands on the bromine-passivated Si(111) surface.

C. The role of Br

It is natural to ask the following questions: What is the role of Br at the interface, and what happens to Br upon annealing? It should be noted that the amount of Br initially present on the Br-passivated Si(111) substrate, well oriented or vicinal, is less than 1 ML.[13,16,19] This is a very small amount of Br compared to the initial thickness of the Au layer. We have not followed what happens to Br during annealing, i.e., during gold silicide growth. We made use of the fact that Br passivation of the Si(111) surface inhibits the growth of oxide on the surface. This facilitates diffusion across the interface which is required for the formation of silicide. For an Au film deposited on a Si(111) surface having oxide, the diffusion across the interface is negligible at the Au-Si eutectic temperature (363 °C). As mentioned above, for samples where Au was deposited on Si(111) surfaces having native oxide, no silicide growth was observed even after annealing at 600 °C for 20 min. It would be interesting to monitor what happens to Br during Au deposition and during gold silicide growth. However, this requires other *in situ* surface-sensitive techniques. This study would be interesting in the light of the recent spurt of activities in the area of surfactant-mediated epitaxial growth,[24] where the surfactant layer floats at the surface of the overlayer. Arsenic and other impurities on silicon surfaces have been used for this purpose.[24,25] A surfactant reduces surface free energy. As passivates the Si(111) surface and reduces the surface free energy. So does Br.

The gold silicide islands in our study are much larger than those obtained on atomically clean surfaces in Ref. 10. The area of our largest islands of uniform width is about four orders of magnitude larger than the area of the largest islands in Ref. 10. It may be noted that the island size may increase in surfactant-mediated growth. [In the extreme cas the growth mode may be changed; for example, the Volmer-Weber (or island growth) mode may be changed to the Frank–Van der Merwe (layer by layer) mode in presence of a surfactant.[24]] However, the origin of the difference in island size (or critical island size) cannot be ascertained, as the initial thicknesses of the Au layers are also quite different in the two studies.

D. Vicinality and the role of steps

We have used commercially available Si wafers for our studies. The surface normal was $(4.0\pm0.5)°$ misoriented from the [111] direction. The wafer had a small cut from which the $[1\bar{1}0]$ direction could be identified. We used (111) x-ray reflection measurements on this wafer for four different azimuthal orientations about the surface normal to identify the misorientation direction, which was found to be toward the $[\bar{1}\bar{1}2]$ direction. In this situation the steps would predominantly run along the $[1\bar{1}0]$ direction.[29] Our large silicide islands are elongated along the $[1\bar{1}0]$ direction, i.e., along the steps. The misorientation of the vicinal Si(111) surface toward the $[\bar{1}\bar{1}2]$ direction reduces step bunching but introduces single- and triple-layer steps.[29] The misorientation angle (4°) of our substrate gives roughly a distance between steps from 5 to 15 nm. So the micrometer-size islands must sprawl across many steps. In this situation one may wonder whether the steps have any role to play for the alignment of the elongated silicide islands. In Ref. 29, it is clearly shown in a scanning tunneling microscopy (STM) picture (Fig. 5 of Ref. 29) that islands can sprawl over many steps, and it is obvious that growth is preferential along the step direction. It is well known that vicinal surfaces of semiconductors are usually used for directed epitaxial growth.[31] There is also evidence of the orientation of a macroscopic epitaxial overlayer being affected by the degree of misorientation or step densities of a vicinal substrate.[32]

E. Gold silicide structure and epitaxy

Gold and silicon form a simple eutectic system with no intermediate phases under equilibrium conditions. However, various metastable phases can be obtained under different growth conditions. Crystalline gold silicide have been studied by many workers. Nevertheless, detailed structures are not available. Various structures have been proposed. Recently, for gold silicide precipitates in silicon an orthorhombic structure with $a = 0.960$ nm,

$b = 0.768$ nm and $c = 0.690$ nm has been proposed by Baumann and Schroeter.[33] However, they could not determine the atomic position in the unit cell. The unit cell is not primitive. They observed that the lattice vector b is aligned with a Si[110] direction. The magnitude of b is just twice (2×0.384 nm) the interatomic distance along the $[1\bar{1}0]$ direction on the ideal Si(111) surface—a favorable condition for epitaxy of the silicide grown on a Si(111) surface. However, this case cannot be compared to our case, as this is not for the eutectic silicide. Green and Bauer studied gold silicide growth in the Au film deposited on a Si(111) surface under UHV conditions.[26] They obtained a silicide composition (17% Si, 83% Au) which is close to the eutectic composition. For films annealed at 360 °C or above they obtained a rectangular unit cell with lateral periodicities of 0.935 and 0.735 nm in the silicide layer. One of these is parallel to the $[1\bar{1}0]$ direction of the Si substrate. (The reported bulk gold silicide structures do not include these periodicities.) Assuming the periodicities $a^{\text{silicide}} = 0.735$ nm and $b^{\text{silicide}} = 0.935$ nm for a silicide grown on a Si(111) surface, the epitaxial relationship may be explored. On an ideal Si(111) surface a rectangular unit cell can be defined with lateral periodicities $a^{\text{Si}} = 0.384$ nm and $b^{\text{Si}} = 0.665$ nm. Therefore, a^{silicide} is 4.3% smaller than $2a^{\text{Si}}$, and $2b^{\text{silicide}}$ is 6.3% smaller than $3b^{\text{Si}}$. Thus the silicide would be under anisotropic tensile stress. The stress would be larger along the b axis. In the case of anisotropic stress the elongated islands would align themselves perpendicularly to the direction of higher stress, i.e., along the a axis, which is what has been observed in Ref. 10 and the present work.

Green and Bauer studied the annealing behavior of thick (10–100 nm) Au films by LEED and Auger electron spectroscopy (AES). They obtained a sandwich structure on the silicon substrate: (i) a thin silicide layer, (ii) an almost pure Au film, and (iii) a top silicide layer (~ 3 nm). We observed no pure Au layer within the probe depth(~ 1 μm) in our EDX analysis. Additional evidence that each island is gold silicide and has a sharp interface with the Si substrate comes from our SIMS studies.[34]

For annealing at higher temperatures (above the eutectic temperature) we also observed the silicide islands, though we have not determined their composition. However, the main changes are the breaking of Au fractal branches and their further agglomeration. Longer (50 and 80 min) annealings, though changing the Au fractal structures, do not have any significant effect on the silicide island structures. In our previous studies we observed some differences in the diffusion behavior of Cu in n- and p-type Si(111) substrates.[21,22] For the Au/Si(111) system we used p-type (B doped, $\rho = 1.5-2.5$ Ω cm) Si(111) substrates as well. All qualitative features observed for the n-type substrate were also observed for the p-type substrate. We made measurements for three different initial Au thicknesses. For the film thicknesses of 116 and 120 nm the results were almost identical. For a smaller film thickness (14 nm) we observed mainly triangular and some trapezoidal silicide islands. No further studies were made on this sample.

IV. CONCLUSIONS

Growth of epitaxial structures of gold silicide has been observed in Au thin films prepared by vacuum evaportion of Au on bromine-passivated Si(111) substrates, and subsequent vacuum annealing at 360 °C. These structures reflect the threefold symmetry of the Si(111) substrate. The small gold silicide islands are of equilateral triangular shapes. These epitaxial triangular islands grow larger up to a certain critical size, beyond which the triangular structures undergo a shape transition to an elongated trapezoidal shape. The shape and energy of the islands have been quantitatively analyzed in light of a recent theory of shape transition. All the elongated islands observed in our study are aligned in the same direction, although one would expect them to grow in three different orientations imposed by the threefold symmetry of the Si(111) substrate surface. The threefold symmetry in the elongated island growth is presumably broken due to the vicinality of the substrate surface. We observed islands with aspect ratios as large as 15:1. However, under appropriate conditions, the islands may grow much longer in the preferential direction. In the scanning electron micrograph of the islands, we found evidence for dislocations in the islands. This implies that both the strain relief mechanisms—the shape transition and the formation of dislocations—are concomitant in the growth of gold silicide islands on a bromine-passivated Si(111) substrate.

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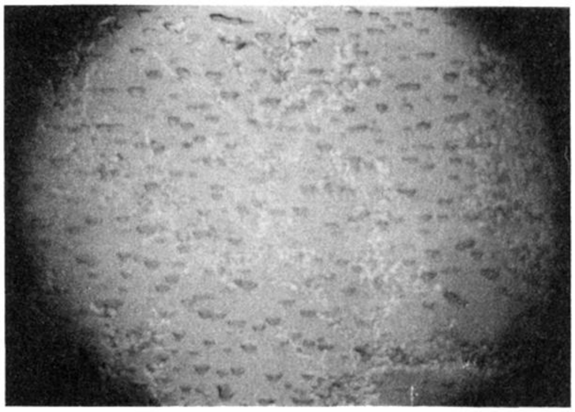

FIG. 1. Photomicrograph showing Au_4Si islands, that is, epitaxial Au_4Si crystallites on the Si(111) substrate. The threefold symmetry is reflected in the shape of many islands. Smaller structures are formed for shorter duration of annealing. The diameter of the image is 400 μm.

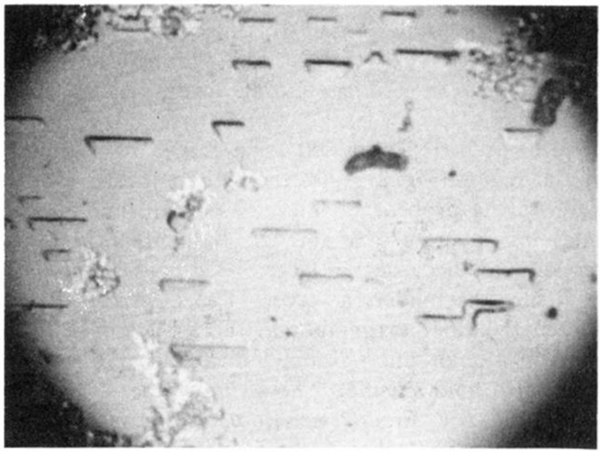

FIG. 2. Au_4Si islands in the shape of a trapezoid. Although the islands vary in length, their width remains practically constant and approximately equal that of the largest triangular islands. The diameter of the image is 400 μm.

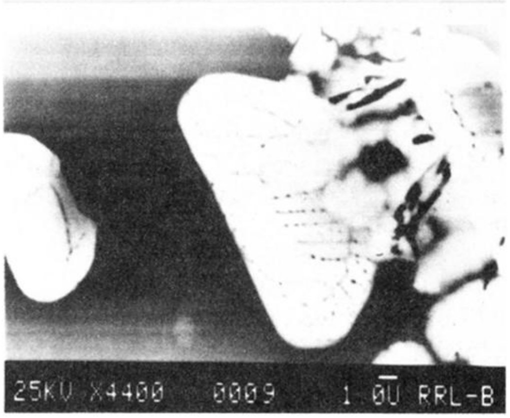

FIG. 4. A scanning electron micrograph showing pin-hole patterns in the strained Au_4Si islands. The length of the middle island is $\approx 20\ \mu m$.