IP/BBSR/93-66

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

K. Sekar, G. Kuri, P. V. Satyam, B. Sundaravel, D. P. Mahapatra and B. N. Dev

Institute of Physics, Bhubaneswar-751005, India

Abstract

Growth of epitaxial gold silicide islands on bromine-passivated Si(111) substrates has been studied by optical and electron microscopy, electron probe micro analysis and helium ion backscattering. The islands grow in the shape of equilateral triangles 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 Si[110] directions. We have observed elongated islands with aspect ratios as large as 8:1. These islands, instead of growing along three equivalent [110] directions on the Si(111) substrate, grow only along one preferential direction. This has been attributed to the vicinality of the substrate surface.

PACS No. : 68.55 - Thin film growth, structure, and epitaxy
. 66.10C - Diffusion and thermal diffusion
. 68.22 - Surface diffusion, segregation and interfacial compound
. formation

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]. Thus shape changes, such as island formation, have been identified as a major mechanism for strain relief. Recently Tersoff and Tromp [5] have 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. But 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 Si(001) surface. Prior to this, various other groups also observed elongated island growth of Ge on Si(001) [6], Au on Ag(110) [7], Au on Mo(111) and on Si(111) [8] and $GaAs$ islands on Si [9]. In all the aforementioned cases where the elongated island growth was observed, the deposition was performed under ultrahigh vacuum (UHV) condition in the submonolayer to a few monolayers range and on atomically clean substrates.

Here we present our observation of the growth of large epitaxial gold silicide islands on Si(111) substrates in a non-UHV method. Moreover, the epitaxial structures were obtained from a relatively thick ($\sim$ 1000 $\mathring{A}$) film deposited uniformly on the substrate. After annealing, we have observed growth of small equilateral triangular silicide islands reflecting the threefold symmetry of the underlying Si(111) substrate. The size of these triangular islands grow up to a critical size beyond which there is a transition to a trapezoidal shape. The trapezoidal islands have varying lengths, but similar widths. The largest of the islands have an aspect ratio of about 8:1. The main observed features are in reasonable agreement with the prediction of the recent theory of shape transition by Tersoff and Tromp [5]. However, in this theory dislocation-free strained islands have been considered. We find evidence for dislocations in the silicide islands as well. Thus, to our knowledge, we report for the first time the evidence for both the strain relief mechanisms, namely, the shape transition and

the formation of dislocations in the same system. Another interesting feature of our observations is that all the elongated islands 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. This additional symmetry-breaking in the growth of epitaxial islands has been attributed to the vicinality of the substrate surface.

The method of sample preparation involves gold evaporation onto a bromine-passivated Si(111) wafer (n-type, Sb-doped, 0.005-0.02 Ωcm) substrate and subsequent annealing. The method used for the bromine passivation of the Si(111) surface is known to provide Br adsorption ($\approx$ 1/4 monolayer) at the atop site on the surface Si dangling bonds on hydrofluoric acid-etched [10] or cleaved [11] Si(111) surfaces. Br adsorption inhibits the surface oxidation process. A detailed x-ray photoelectron spectroscopic characterization of the Br-treated Si surfaces has been published elsewhere [12]. It was also shown that a Cu thin film deposited on a Br-passivated Si(111) surface has interdiffusion behavior very similar to the case where Cu was deposited on an atomically clean (7×7) reconstructed Si(111) surface [13,14]. It should be noted that chemically prepared Br-passivated $Si(111)$ surface in open air [10] and Br-adsorbed atomically clean $Si(111)$ surface under ultrahigh vacuum condition [15] show identical behaviour regarding Br-adsorption site, $Si-Br$ bond length, substrate surface relaxation etc. Also the presence of some impurities on the Si substrate prior to metal deposition is not an impediment for epitaxial silicide growth. In this case the concept of self-cleaning interface has been discussed by Lau and Mayer [16]. Epitaxial growth on Br-passivated substrate assumes futher importance in the light of the recent spurt of activities on impurity (surfactant)-controlled epitaxial growth [17]. In the present work a 1200 $\mathring{A}$ thin Au film was evaporated from a W basket onto a Br-passivated Si(111) substrate at room temperature in high vacuum (10^{-6} Torr). Then the sample was annealed at (360$\pm$10)^{o}C, that is around the $Au-Si$ eutectic temperature of 363^{o}C [18], for 20 minutes in high vacuum. This gave rise to the triangular and trapezoidal island structures shown in Fig. 1 and Fig. 2. The triangular islands have strong similarities with the growth of (7×7) reconstructed triangular domain growth on an atomically clean Si(111)

surface in the low temperature phase of the $(7 \times 7) \leftrightarrow (1 \times 1)$ order-disorder transition [19]. We also observed fractal structures of Au for this system which will be presented elsewhere [20]. Longer (50 min and 80 min) annealing, though changes the Au fractal structure, does not have any significant effect on the large silicide island structures.

In Fig. 1, we notice the formation of the equilateral triangular structure reflecting the three-fold symmetry of the Si(111) surface. This indicates that these triangular islands are crystalline − epitaxially grown on the substrate. The composition of the triangular structures, as determined from electron probe micro analysis (EPMA), is Au_4Si [actually $(79\pm 3)\%Au$, $(21 \pm 3)\%Si$ for both triangular and trapezoidal islands]. Here we observe equilateral triangles of almost identical size. The edges of the equilateral triangles are aligned along substrate [110] directions. This alignment has also been observed for silicide growth on a $Si(111)$ surface under UHV condition [8] as well as for gold silicide precipitates in the bulk [21]. 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 triangles. The widths of all the trapezoidal islands are comparable and are roughly equal to the width of the largest equilateral triangular island. That is, growth of the islands beyond a critical size, represented by the largest triangular island, is associated with the shape transition: triangle to trapezoid.

We will discuss our results in the light of the recent theory given by Tersoff and Tromp [5], 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 :

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

where s, t and h are width, length and height of the island, respectively; $\phi = e^{-3/2}cot\theta, \theta$ being the contact angle; Γ contains the surface and interface energies; 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 $s = t = \alpha_o$, where

$$\alpha_o = e\phi h e^{\Gamma/ch} \quad (2)$$

For island sizes $s, t < e\alpha_o$, the square island shape ($s = t$) is stable. Once the island grows beyond its optimal diameter α_o 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 abovementioned treatment was for epitaxial islands on a Si(100) surface which has a four-fold symmetry. In this case the island growth up to the critical size has a four-fold symmetry (square). Beyond the critical size the islands grow in rectangular shape. The long rectangular islands have been called self-assembling quasi-one dimensional "quantum wires". In our case the substrate, $Si(111)$, has three-fold 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 submicron size and may be called self-assembling quasi-zero dimenional "quantum dots".

The thickness of the Au_4Si islands is $\sim 1\mu m$, which is estimated from the penetration depth of 10 and 25 keV electrons used for the EPMA composition analysis. The tree-like structures in Fig. 1 consist of Au.

At this point let us try to make some quantitative estimates from the triangular and the trapezoidal islands observed in our experiments. Fig. 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 ($l_1 = l_2 = l_o$) 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 $\sqrt{3}l_o^2/4 = 110\mu m^2$ (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, $e^2\alpha_o^2 = 110\mu m^2$. This provides $\alpha_o = 3.86\mu m$. With $h = 1\mu m$ and assuming $\theta = 45^o$, 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) [22]. 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. [5], the magnitude of the discontinuity must be too small to be detected in the present experiment.

In the low energy electron microscopy (LEEM) study of gold silicide growth on $Si\{111\}$ for submonolayer Au deposition, Mundschau et al. [8] observed triangular island growth for low coverages and rod shaped island growth at higher coverages with the major axis of these rods aligned along $Si[110]$ directions. The rod-like islands had an aspect ratio of $\sim 8:1$. However, in their study they found the elongated islands to be aligned along the three [110] directions on $Si\{111\}$ as expected from the symmetry. Our observation of unidirectional elongated island growth along the $[0\bar{1}1]$ direction may be explained from the fact that our substrate surface was vicinal, i.e., the (111) surface was misoriented by 4^o towards $[2\bar{1}\bar{1}]$ azimuthal direction. This misorientation gives rise to the formation of single-layer and triple-layer steps which run along the $[0\bar{1}1]$ direction [23]. Thus our observed elongated islands are along the length of the steps. It is well known that nucleation and growth are predominant at surface defects. In our case the growth might have occured preferentially at the steps. Vicinal surfaces of semiconductors are usually used as substrates for epitaxial overgrowth (such as directed epitaxy) and new interesting electronic properties

of these systems have been predicted [24].

Rutherford backscattering of 2 MeV He^+ ions from the sample provided evidence for the presence of a thin ($\sim$ 50 $\mathring{A}$) layer containing gold even in the island-free region (the apparently depleted flat region in Fig. 2). From EPMA analysis of this region we could not determine whether this Au exists as Au_4Si, because the high energy electrons penetrate much deeper into the sample and leads to overestimation of the Si content. For Au deposition (100-1000 $\mathring{A}$) on Si at room temperature, followed by annealing at $T \leq 400^oC$, and studied by other techniques, such as AES, a continuous silicide layer thickness of $\sim 30\mathring{A}$ was previously reported [25]. In our optical color micrograph the flat region and the islands appear to be of the same color which points to a composition of Au_4Si for the flat region as well. If this thin Au_4Si layer is epitaxial, it would amount to a layer-plus-island or Stranski-Krastanov growth of Au_4Si. The composition of the stringy structure in Fig. 2 as determined by EPMA is 100% Au.

The detailed features of the Au_4Si islands are not visible in the optical micrographs shown in Fig. 1 and Fig. 2. A scanning electron micrograph is shown in Fig. 4. The patterns with pin-hole structures on the islands indicate the presence of dislocations. In fact, in some cases we observed porous structure of 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 Au_4Si islands. As Tersoff and Tromp [5] point out, a partial strain relief through dislocations would not affect the general aspects of shape transition except for reducing the effective value of bulk stress of the island material. One would, of course, expect to see a larger critical size for islands with higher dislocation density. This might be partly responsible for the large size (area $\sim$1000 times those observed in Ref.8) of the gold silicide islands on the bromine-passivated Si(111) surface.

On the Si(111) substrates with a thin oxide layer we did not observe epitaxial island growth upon Au deposition and subsequent annealing at 360^o C. It has been previously shown that the diffusion behavior is different for a metal layer deposited on a bromine-treated Si(111) substrate and on an Si(111) substrate with a native oxide layer, the bromine-

treated substrate behaving like an atomically clean substrate and the native oxide acting as a diffusion barrier at the interface [13].

In conclusion, growth of epitaxial structures of Au_4Si has been observed in Au thin films prepared by vacuum evaporation of Au on bromine passivated Si(111) substrates and subsequent vacuum annealing at 360^{o}C. These structures reflect the threefold symmetry of the underlying Si(111) substrate. The epitaxial structures are of equilateral triangle in shape. These epitaxial triangular islands grow bigger up to a certain critical size. Beyond the critical size the triangular structures undergo a shape transition to an elongated trapezoidal shape. All the elongated islands 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 apparently broken due to the vicinality of the substrate surface. We observed islands with aspect ratios as large as 8:1. 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. This implies, both the strain relief mechanisms − the shape transition and the formation of dislocations − are concomitant in the growth of Au_4Si islands on a bromine-passivated Si(111) substrate. This may be, after all a general feature in the growth of strained epitaxial islands.

ACKNOWLEDGMENTS

We thank Prof. Pham V. Huong and Dr. M. Lahaye for some of the EPMA measurements and Dr. B. K. Mohapatra for taking the scanning electron micrograph.

REFERENCES

[1] PEARSAL T. P., *Critical Reviews in Solid State and Materials Sciences*, **15**, (1989) 551.

[2] VAN DER MERWE J. H., *J. Appl. Phys.* **34**, 117 (1963); **34**, (1963) 123.

[3] MATHEWS J. W. and BLAKESLEE A. E., *J. Crys. Growth*, **29**, (1975) 273; **32**, (1976) 265.

[4] SPENCER B. J., VOORHEES P. W. and DAVIS S. H., *Phys. Rev. Lett.* **67**, (1991) 3696.

[5] TERSOFF J. and TROMP R. M., *Phys. Rev. Lett.* **70**, (1993) 2782.

[6] MO Y.-W., SAVAGE D. E., SWARTZENTRUBER B. S. and LAGALLY M. G., *Phys. Rev. Lett.* **65**, (1990) 1020.

[7] ROUSSET S., CHIANG S., FOWLER D. E. AND CHAMBLISS D. D., *Phys. Rev. Lett.* **69**, (1992) 3200.

[8] MUNDSCHAU M., BAUER E. and TELIEPS W., *Surf. Sci.* **213**, (1989) 381.

[9] PONCE F. A. and HETHERINGTON C. J. D., in *Proceedings of the Forty-Seventh Annual Meeting of the Electron Microscopy Society of America*, edited by G. W. BAILEY, (San Franscisco Press, San Francisco, CA, 1989) p.586; AKIYAMA M., UEDA T. AND ONOZAWA S., *Meter. Res. Soc. Symp. Proc.* **116**, (1988) 79.

[10] GOLOVCHENKO J. A., PATEL J. R., KAPLAN D. R., COWAN P. L., ; BEDZYK M. J., *Phys. Rev. Lett.* **49**, (1982) 560 and MATERLIK G., FRAHM A. and BEDZYK M. J.,*Phys. Rev. Lett.* **52** (1984) 441.

[11] DEV B. N., ARISTOV V., HERTEL N., THUNDAT T. and GIBSON W. M., *Surf. Sci.* **163**, (1985) 457.

[12] SEKAR K., KURI G., MAHAPATRA D. P., DEV B. N., RAMANA J. V., SANJIV KUMAR and RAJU V. S., *Surf. Sci.* **302** (1994) 25..

[13] SEKAR K., SATYAM P. V., KURI G., MAHAPATRA D. P. and DEV B. N., *Nucl. Instr. and Meth.* **B71**, (1992) 308.

[14] SEKAR K., SATYAM P. V., KURI G., MAHAPATRA D. P. and DEV B. N., *Nucl. Instr. and Meth.* **B73**, (1993) 63.

[15] FUNKE P. and MATERLIK G. *Surf. Sci.* **188** (1987) 378.

[16] LAU S. S. and MAYER J. W., in *Treatise on Materials Science and Technology*, Vol. **24**, K. N. TU and R. ROSENBERG (Eds.), Academic Press, 1982, pp 92-93.

[17] EAGLESHAM D. J., UNTERWALD F. C. and JACOBSON D. C., *Phys. Rev. Lett.* **70**, (1993) 966 and references therein.

[18] JOHNSON ALAN A., *Solid State Comm.* **76**, (1990) 773.

[19] TELIEPS W. and BAUER E., *Surf. Sci.* **162**, (1985) 163.

[20] SEKAR K., SATYAM P. V., KURI G., MAHAPATRA D. P. and DEV B. N., *IP/BBSR/92-56* (to be published).

[21] BAUMANN F. H. and SCHROETER W., *Phil. Mag. Lett.* **57**, (1988) 75.

[22] For the triangular islands, assumption of $s = t = \sqrt{A}$ yields E/V values which deviate by $\sim 1\%$ from the curve shown in Fig. 3(a).

[23] See for example, HANDBUECKEN M., ROETTGER B., KLIESE R., VIANEY I. and NEDDERMEYER H., *Europhys. Lett.* **23**, (1993) 573; PHANEUF R. J. and WILLIAMS ELLEN D., *Phys. Rev.* **B41**, (1990) 2991.

[24] See for example, P. M. PETROFF, in *Kinetics of Ordering and Growth at Surfaces*, edited by M. G. LAGALLY (Plenum Press, New York, 1990) p. 245 and other articles

therein.

[25] LE LAY G., *Surf. Sci.* **132**, (1983) 169.

FIGURES

FIG. 1. Photomicrograph showing Au_4Si islands, that is, epitaxial Au_4Si crystallites on the Si(111) substrate. The three-fold symmetry is reflected in the shape of many islands. Smaller structures are formed for shorter duration of annealing. Diameter of the image is $400\mu m$.

FIG. 2. Au_4Si islands in the shape of trapezoid. Although the islands vary in length, their width remains practically constant and approximately equal to that of the largest triangular islands. Diameter of the image is $400\mu m$.

FIG. 3. (a) Computed energy per unit volume of island, in units of ch/α_o, vs measured island area A ($\circ$- triangle, $\star$- 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. Unit of length for l_1 and l_2 is α_o and that of A is α_o^2 [see text and Equ.(2)]. Solid lines are to guide the eye. For $A < e^2\alpha_o^2$, 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 $\approx 20\mu m$.