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Influence of patterning on the nucleation of Ge islands on Si and SiO_2 surfaces

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Surface patterning is expected to influence the nucleation site of deposited nanostructures. In the present study, clean Si and SiO_2 surfaces were patterned by a nanolithographic process using a Focused Ion Beam (FIB). Ge was evaporated in Ultra High Vacuum at 873 K on these substrates, resulting in the formation of island arrays. Based on scanning tunneling microscopy (STM) and atomic force microscopy (AFM) images, a statistical analysis was performed in order to highlight the effect of patterning on the size distribution of islands compared to a non patterned surface. We find that the self-organization mechanism on patterned substrates results in a very good arrangement and positioning of Ge nanostructures, depending on growth conditions and holes distance, both on Si and SiO_2 surfaces.

Quantum dots (QDs) grown on semiconductor surfaces represent an important area of focus for applications in nanotechnology. The heteroepitaxial self assembling of 3-D islands holds the promise of an easy route to fabricate QDs for future electronic applications [1]. The production of nanomemories based on Ge islands on Si substrates requires the growth of nanocrystalline islands embedded in a well characterized SiO_2 layer [2, 3]. In fact the quality of the oxide tunnel barrier affects greatly the working characteristics of the memory device such as the retention time, dot charging and stacking capability [4].

Moreover, to improve the performance of electronic devices, considerable effort has to be devoted to control the size uniformity, density and positioning of the self assembled nanostructures [5-10]. Different techniques have been developed to achieve long-range ordering of islands with a very narrow size distribution in the case of Ge/Si(001) systems, such as growth of stacked multilayers of heteroepitaxial islands [11, 12] or deposition of thin relaxed films of SiGe [13, 14]. Recently very interesting results have been obtained by using a combination of self-assembling QDs growth and pre-patterning of substrates [15-19] on a length scale where conventional lithographic techniques [20-22] are no longer applicable. Two different routes have been taken towards nanopatterning: one, artificial, based on the development of new patterning techniques with nanometer resolution, such as high resolution electron lithography [6, 7, 9, 20-22] or STM nanolithography [23-25] and the other one which takes advantage of ordered patterns occurring spontaneously [26-28] in certain conditions of temperature or substrate stress. We have recently proposed two natural approaches to control Ge island positioning, one based on step bunching instabilities which spontaneously occur on Si(111) during direct current annealing [29] and the other one in which nanostructuring is induced by Ge deposition on misoriented Si(001) surfaces [30]. However, these methods are still unreliable for the applications, since either uniformity or sizes of the islands don't match the high standards required in nanoelectronics. Also, in nanolithography the shape and size of the single hole plays an important role to stabilize the quantum dots that are nucleating in the nearby region or at its edge [21]. For this reason a detailed study of island nucleation and growth on substrates with a dense patterning is required.

Experimental

In the present paper we report new results on growth and arrangement of Ge islands on Si surfaces patterned by using Focused Ion Beam (FIB) [31, 32] at different densities. Two kinds of patterned surfaces were studied: a bare Si(001) surface and a 5 nm thick SiO_2 layer grown on Si(001) substrate. In the first case, we followed, in real time, the growth of Ge nanostructures using a Scanning Tunnelling Microscope (STM). We established **the distribution size** and the influence of patterning on Ge growth. In the second case, we used an Atomic Force Microscope (AFM) to study the distribution of Ge droplets generated, after thermal annealing, on an amorphous layer.

FIB patterned samples were produced by FEI Company. Their Dual Beam System FIB uses a liquid metal ion source to generate a Ga^+ ion beam (I**Error! Not a valid embedded object.**1 pA, V=5-25 keV) at normal incidence and at a very low distance from the sample surface. After FIB patterning, the Si(001) samples undertook a cleaning treatment in an ultrasonic bath of diluted HCl (1:10) followed by a rapid thermal annealing at 1300 K for 1 minute in N_2 atmosphere to remove Ga atoms embedded in the Si matrix. The measured concentration of Ga after this treatment was below $4x10^{16}$ at.cm^{-3}. Then, a new annealing in Ultra High Vacuum at 873 K for 30 minutes was carried out in order to get rid of residual contaminations. Images of the array of holes in UHV have been obtained by STM immediately after this treatment as a final check (Fig. 1a)

In the case of the oxidized samples, a two step process allows to obtain a 5 nm thin patterned oxide samples [19, 32].

Ge was deposited on the surface in Ultra High Vacuum ($p \leq 3\ 10^{-10}$ Torr). On the Si(001) bare substrate kept at 873 K, Ge was deposited with a flux of 0.13 ML/min; on the oxidized samples, Ge was deposited at room temperature and then annealed at 1000 K for one hour.

Clean Si(001) substrates.

Two different arrays of pits with depth of 30 nm, diameter of 150 nm and a periodicity of 780±30 nm and 500±30 nm, respectively, have been produced on the Si(001) bare substrates. On these surfaces we have followed in real-time the Ge growth at a temperature of 873 K. As displayed in Fig. 1 (2.5 ML),

the nucleation starts nearby a hole and develops into a Ge island covering the entire pit. This occurs in most cases, producing a nicely ordered pattern at 8 ML coverage. In Fig. 2, Si(001) surfaces with two different pitches of 780 and 500 nm are visualized after 8 ML of Ge coverage. The increased islands density in the sample with smaller pitch is evident. In particular in the case of large pattern (Fig. 2a), the island density is measured equal to 1.9×10^8 islands·cm^{-2} close to the holes density 1.7×10^8 holes·cm^{-2} while, for the second pattern (Fig. 2b) with a density of holes of 4×10^8 holes·cm^{-2}, the islands density is about 3.4×10^8 cm^{-2} . It is evident how the islands pattern follows strictly the holes pattern.

After 20 ML Ge deposition (Fig 3a) the difference in ordering between non-patterned (Fig. 3b) and patterned area (Fig. 3c) is evident. The density of the islands on the patterned region is estimated to 2.1×10^8 islands·cm^{-2}. The Fast Fourier Transform (FFT) made on these two selected regions evidences the different degree of ordering outside and inside the patterned area. As a result the FFT analysis allows to measure a well-defined periodicity for Ge islands equal to 790±50 nm on the patterned region, while, outside, the FFT doesn't show any spot demonstrating the absence of lateral ordering where arrays of pits are not present.

The statistical analysis of the diameters of islands nucleated on patterned and non-patterned areas offers another interesting issue. From the Gaussian fit (Fig. 3d), a mean diameter of 280 nm is found for islands grown on the unpatterned surface, whereas for the islands grown on the patterned surface, a bimodal distribution with two peaks at 80 nm and 285 nm appears. A further analysis of the islands grown on the patterned surface (Fig. 4), by discriminating islands nucleated in correspondence or between the holes, has been performed. We found a single peak at 280 nm for islands corresponding to holes, and we note that the same value was previously obtained for islands randomly nucleated on the unpatterned region. We conclude that the patterning does not affect the growth mode but strongly affects the lateral ordering of islands. Moreover, as displayed by the size distribution in Fig. 4, we evidence that the double peak on the patterned surface results from the nucleation of islands in between the holes. The peak at 90 nm corresponds to the formation of a further generation of islands

drawing the residual Ge available on the substrate [25]. This effect can be reduced by reducing the pitch of the array to that of the collection area for the formation of a pyramid [21], since the mean free path of Ge atoms is limited [33].

SiO_2 substrates

To study the patterning effect on Ge growth on SiO_2, dense holes arrays ($4x10^{10}$ holes·cm^{-2}) were produced by FIB on oxidized Si. In this case, a double procedure of oxidation and chemical etching has been undertaken, in order to develop a 5 nm clean SiO_2 layer presenting a patterned surface.

A first experiment consists in depositing 5.2 ML of Ge at 873 K. The surface (Fig. 5a) displays randomly nucleated islands on a patterned SiO_2 surface. Some islands seem nucleate inside the holes, other nearby. Some regions are free of islands. Nevertheless, a mean diameter of 32 nm is extracted from the size distribution. At this growth temperature, the surface topography does not play a crucial role and does not affect the lateral ordering.

For a second experiment, Ge was deposited at room temperature to form an amorphous layer that is subsequently annealed at high? temperature (773 K) for 20 min to form Ge droplets. On a non-patterned region of the surface, after 4.8 ML Ge deposition, the nanostructures, with a density of $4.1x10^{10}$ islands.cm^{-2}, cover homogeneously the surface without lateral ordering (Fig. 5b). The size distribution is bimodal with two diameters of 24 nm and 31 nm. On patterned regions, (Fig 5c) Ge droplets, with a density of $3.5x10^{10}$ islands.cm^{-2}, exhibit a very good ordering. The diameter distribution displays three peaks: the largest at 47 nm and the other two peaks at 26 nm and 35 nm (Fig 5c). These latter peaks correspond to those obtained on the non patterned area whereas the 47 nm one is close to the pitch value. These results suggest that the patterning favours first of all the formation of nanostructures, with the same periodicity of pits, which reach a larger size. Moreover, the shape of the distribution, especially the trail, points out that a transition toward larger nanostructure occurs, i.e. the annealing time was not longer enough for the Ge droplets to achieve completely their equilibrium shape.

In summary, we have shown that the FIB patterning of Si and SiO_2 surfaces affects the nucleation sites of Ge nanostructures deposited, increasing both ordering and homogeneity of the islands. A good matching is obtained between the density of the original array of pits and the resulting arrays of Ge droplets. A real time STM study confirms that pyramids nucleate nearby the pits and then, by increasing their size, the island transformed in dome covers the pits. From the analysis of the size distribution, we established that a second set of islands develop in between the pits at large coverage, showing that the patterning affects lateral ordering but not the growth mode. In the case of a SiO_2 surface, patterning drives Ge to form a well-ordered array of droplets after thermal annealing.

We can conclude that the ordered distribution of pits produced by FIB is an efficient template to obtain ordered arrays of QDs. Our results suggest also that it is possible to shrink the size distribution of islands by exploiting the diffusion length of the atoms on the surface, using the right combination of the array pitch and growth temperature.

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References

[1] J. Stangl, V. Holy, G. Bauer, Rev. Mod. Phys. **76** (2004) 725.

[2] P.W. Li, D. M. T. Kuo, W. M. Liao, W.T. Lai, Appl. Phys. Lett. **88** (2006) 213117.

[3] I. Berbezier, A. Karmous, A. Ronda, A. Sgarlata, A. Balzarotti, P. Castrucci, M. Scarselli, M. De Crescenzi, Appl. Phys. Lett. (2006) in press.

[4] Y. Liu, S. Tang, S. K. Banerjee, Appl. Phys. Lett. **88** (2006) 213504.

[5] N. Deng, P. Chen, Z. Li, J. Crystal Growth **263** (2004) 21.

[6] J.L. Gray, N. Singh, D.M. Elzey, R. Hull, J.A. Floro, Phys. Rev. Lett. **92** (2004) 135504.

[7] M. Goryll , L. Vescan, H. Lüth, Mater. Sci. Eng. B **101** (2003) 9.

[8] Zhenyang Zhong, A. Halilovic, T. Fromherz, F. Schäffler, G. Bauer, Appl. Phys. Lett. **82** (2003) 4779.

[9] L. Vescan, T. Stoica, J. Appl. Phys. **91** (2002) 10119.

[10] L. Vescan, K. Grimm, M. Goryll, B.Höllander, Mater. Sci. Eng. B **69** (2000) 324.

[11] O.G. Schmidt, N.Y. Jin-Phillipp, C. Lange, U.Denker and K. Eberl, R. Schreiner, H. Gräbeldinger, H. Schweizer, Appl. Phys. Lett. **77** (2000) 4139.

[12] G. Capellini, M. De Seta, C. Spinella, F. Evangelisti, Appl. Phys. Lett. **82** (2003) 1772.

[13] Y.H. Xie, S.B. Samavedam, M. Bulsara, T.A. Langdo, E.A. Fitzgerald, Appl. Phys. Lett. **71** (1997) 3567.

[14] S.Yu Shiryaev, F. Jensen, J. L. Hansen, J. W. Petersen, A. N. Larsen, Phys. Rev. Lett. **78** (1997) 503.

[15] C.Teichert, C. Hofer, K. Lyutovich, M. Bauer, E. Kasper, Thin Solid Film **380** (2000) 25.

[16] J.J. Metois, S. Stoyanov, Surf. Sci. **440** (1999) 407.

[17] I. Berbezier, A. Ronda, A. Portavoce, N. Motta, Appl. Phys. Lett. **83** (2003) 4833.

[18] P.D. Szkutnik, A. Sgarlata, N. Motta, A. Balzarotti, Phys. Rev. B **69** (2004) 201309.

[19] A. Karmous, I. Berbezier, A. Ronda, Phys. Rev. B **73** (2006) 75323.

[20] T.I. Kamins, R. Stanley Williams, Appl. Phys. Lett. **71** (1997) 1201.

[21] E.S. Kim, N. Usami, Y. Shiraki, Appl. Phys. Lett. **72** (1998) 1618.

[22] G. Jin, J.L. Liu, Y.H. Luo, K.L.Wang, Thin Solid Film **380** (2000) 169.

[23] S. Kohomoto , H. Nahamura, T. Ishigawa, K. Asahava, Appl. Phys. Lett. **75** (1999) 3488.

[24] Zhenyang Zhong, G. Bauer, Appl. Phys. Lett. **84** (2004) 1922.

[25] Zhenyang Zhong, A. Halilovic, M. Mülberger, F. Schäffler, G. Bauer, J. Appl. Phys. **93** (2003) 6256.

[26] H. Omi,. T. Ogino, Thin Sol. Film **369** (2000) 88

[27] F.K. Men, Feng Liu, P.J. Wang, C.H. Chen, D.L. Cheng, J.L. Lin, F.J. Himpsel, Phys. Rev. Lett. **88** (2002) 096105.

[28] I. Berbezier, A. Ronda, F. Volpi, A. Portavoce, Surf. Sci. **531** (2003) 231.

[29] A. Sgarlata, P.D. Szkutnik, N. Motta, F. Rosei, A. Balzarotti, Appl. Phys. Lett. **83** (2003) 4002.

[30] P.D. Szkutnik, A. Sgarlata, A. Ronda, N. Motta, I. Berbezier, A. Balzarotti, to be published.

[31] L.R. Harriott and R. Hull in "Introduction to Nanoscale Science and Technology " Ed.by M. Di Ventra, S. Evoy and J.R. Heflin Jr, Kluwer Academic Publ. 2004; ISBN : 1-4020-7720-3

[32] A. Karmous, A. Cuenat, A. Ronda, I. Berbezier, S. Atha, R. Hull, Appl. Phys. Lett. 85 (2004) 6401.

[33] F. Ratto, A. Locatelli, S. Fontana, S. Kharrazi, S. Ashtaputre, S. K. Kulkarni, S. Heun, F. Rosei, Phys. Rev. Lett, **96** (2006) 096103.

[34] A. Sgarlata, A. Balzarotti, I. Berbezier, P. Szkutnik, F. Rosei, N. Motta, IEEE Proc. ICONN 06 Conference (3-7 July 2006 Brisbane Australia).

Figure captions

Figure 1: Sequence of STM images (4.5 µm x 2.5 µm) recorded in real time during Ge deposition at 873 K on a FIB patterned Si(001) substrate with a 780 nm pitch, starting from the clean surface up to 6.5 ML coverage.

Figure 2: STM images (5 µm x 5 µm) for 8 ML deposition of Ge on Si(001) patterned surface with pitch values of (a) 780 nm and (b) 500 nm, respectively.

Figure 3: (a) STM image (18 µm x 18 µm) after 20 ML of Ge deposited at 873 K on a FIB patterned region of a Si(001) surface with a pitch of 780 nm, the dash line separates the patterned from the unpatterned area; (b) zoom (5µm x 5µm) on the unpatterned area and the Fast Fourier transforms of the images; (c) **z**oom (5µm x 5µm) on the patterned area and the Fast Fourier transforms of the images; (d) **d**iameter distributions of the islands for the two regions.

Figure 4: STM image (5 µm x 5 µm) after 20 ML of Ge deposited at 873 K on a FIB patterned Si(001) surface with a pitch of 780 nm with the corresponding diameter distributions of the islands. Circles highlight the islands grown between pits and squares those grown over a pit.

Figure 5: (a) STM image (1 µm x 1 µm) after 5.2 ML of Ge deposited at 873 K on a FIB patterned SiO_2/Si(001) surface with a pitch of 50 nm. At the right, the size distribution. AFM image (1 µm x 1 µm) after 4.8 ML of Ge deposited at room temperature followed by a thermal annealing at 773 K during 20 min on a 5 nm SiO_2/Si(001) surface; view on the same sample of (b) the non patterned region and (c) the patterned region with a pitch of 50 nm. The corresponding diameter distributions are shown on the right panels.

Figure 1

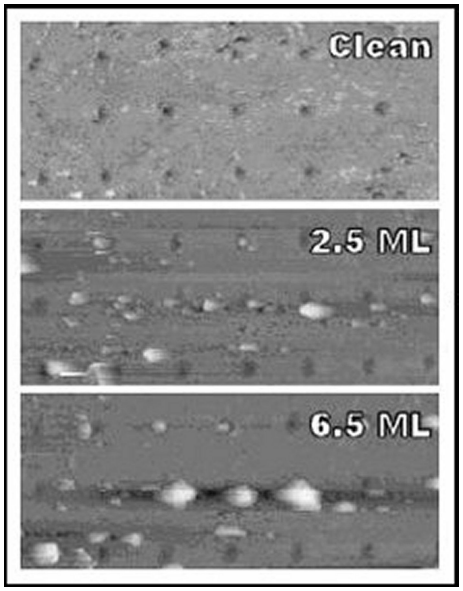


Figure 2

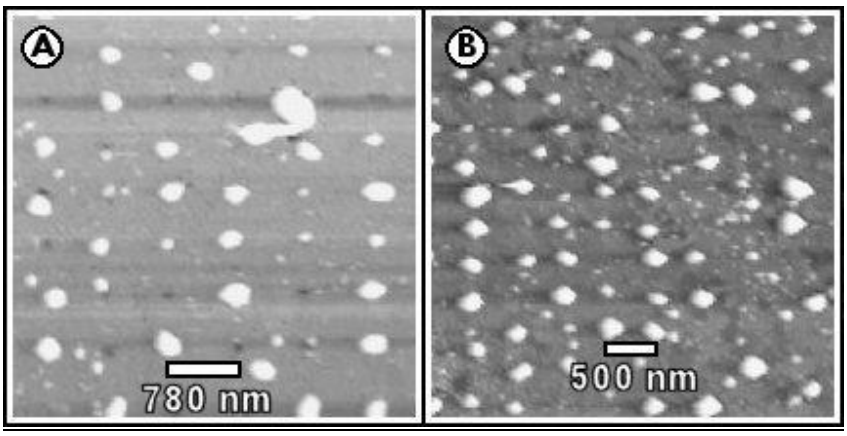


Figure 3

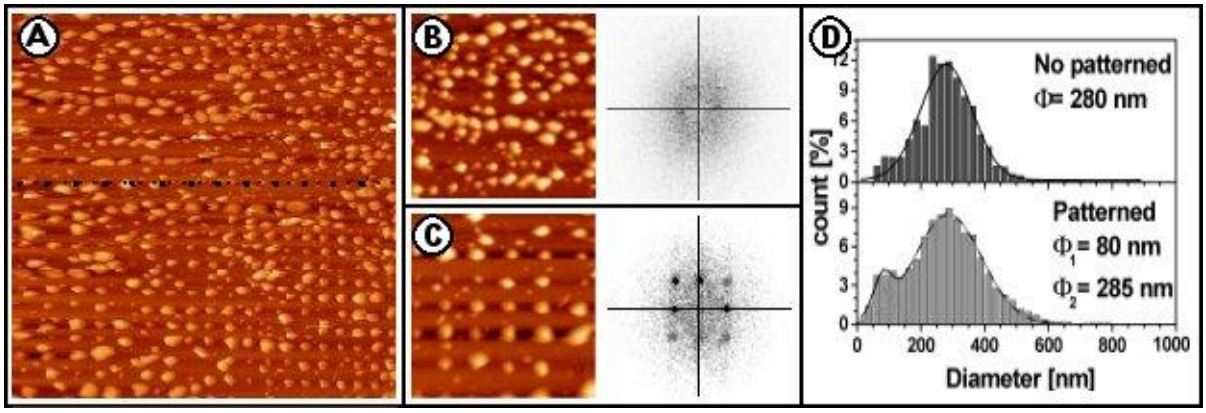


Figure 4

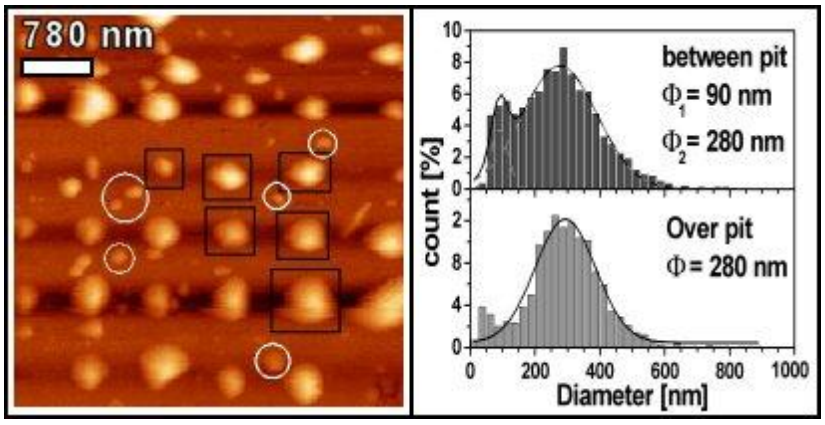
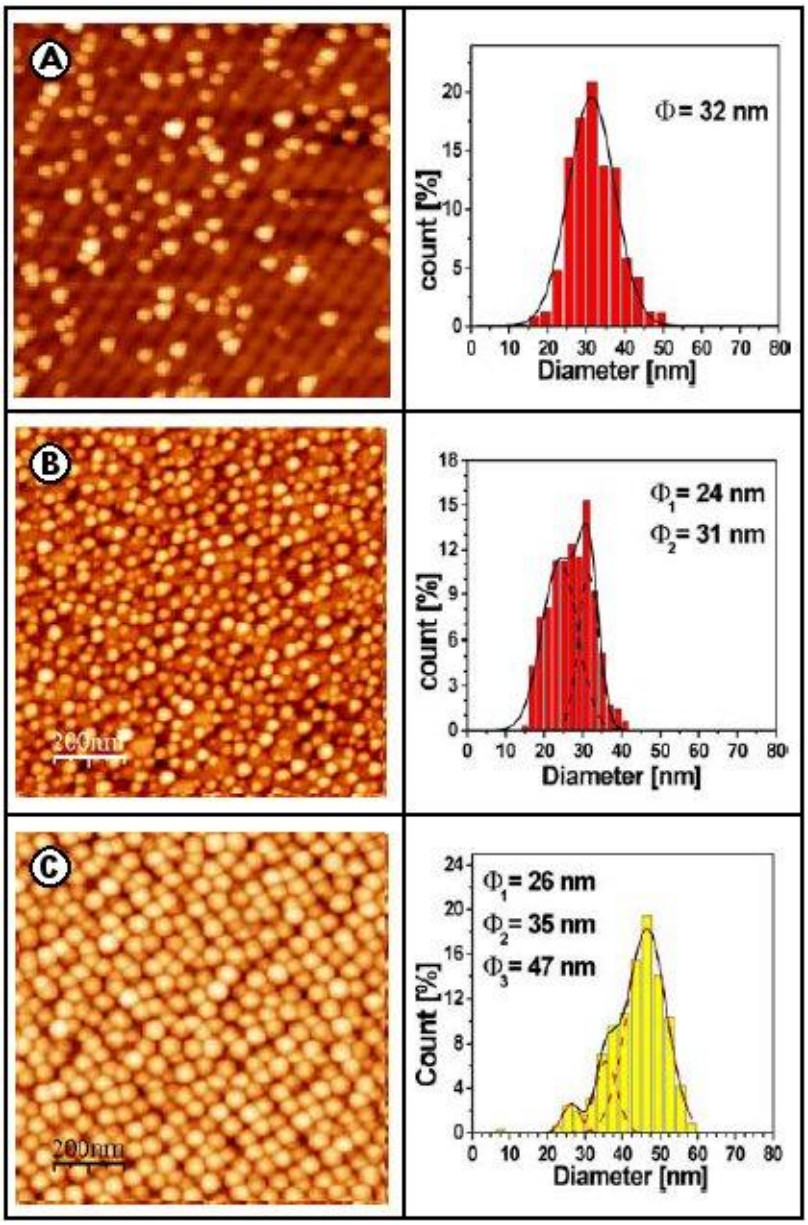


Figure 5


A
Φ = 32 nm
count [%]
Diameter [nm]
B
200nm
Φ1 = 24 nm
Φ2 = 31 nm
count [%]
Diameter [nm]
C
200nm
Φ1 = 26 nm
Φ2 = 35 nm
Φ3 = 47 nm
Count [%]
Diameter [nm]