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Growth of Silicon Nanoclusters on Different Substrates by Plasma Enhanced Chemical Vapor Deposition

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RESEARCH ARTICLE

We report an atomic force microscopy study of the early stages of growth of silicon nanoclusters formed on different substrates by plasma-enhanced chemical vapor deposition, using dichlorosilane (SiH_2Cl_2) and hydrogen (H_2) as reactive gases. (100) *n*-type single crystalline silicon, fused silica, amorphous silicon nitride and corning glass, were used as substrates for the growth of the nanoclusters, which were formed at low substrate temperature (200 °C). The diameter, height and number density of the clusters were controlled by the deposition time and pressure. It was found that not only the plasma conditions but also the surface characteristics of the substrate influence the cluster density, shape, and size. For the ordered silicon surface and the amorphous fused silica, the nanoclusters result oval in shape and exhibit preferential growth along the surface. When deposited over amorphous silicon nitride and corning glass, the density of nanoclusters increases and there is a tendency toward columnar growth since the diameter of the nanoclusters tends to decrease. We conclude that although the specific features of the nanoclusters originate from the chlorine chemistry introduced by the SiH_xCl_y deposition precursor and the chemical stability of chlorine-terminated surfaces under hydrogen plasma, the surface quality and roughness also plays an important role on the nucleation and mobility of the species. The combination of both effects gives rise to the different nanostructured growths observed.

Keywords: Silicon Nanoclusters, Growth, Substrates, PECVD.

1. INTRODUCTION

Silicon nanoclusters (nc-Si) and nanometric-sized silicon structures have attracted a great interest due to their unique properties and applications caused by quantum confinement effects.[1–5] The preparation of nc-Si on different silicon-based substrates or embedded in different silicon-based matrixes, by using plasma enhanced chemical vapor deposition (PECVD) methods, which are widely used in the modern silicon microelectronic industry, has an enormous potential for the development of novel, low-cost and functional Si-based optoelectronic devices.[6,7] Many recent works have been oriented toward the study of the influence of the specific PECVD method, silicon precursor, and experimental conditions used for the preparation of the nc-Si, on their size, size distribution, number density, and properties, in order to control the efficiency, functionality, and reliability of these Si quantum-confined structures.[8–13] Some of these works have demonstrated that the use of low temperature PECVD from chlorinated silicon precursors such as SiH_2Cl_2 or $SiCl_4$ has some advantages for controlling the number density and size distribution of the nc-Si.[12–13] However, there are relatively few studies on the nucleation stage and growth kinetics of nc-Si formed by means of PECVD, and/or the influence of the substrate on the characteristics of these nc-Si.[14–17] Understanding these processes is essential to control the size and number density of nc-Si, thus influencing their quantum properties.

In this paper we have prepared nc-Si on different substrates at low temperature (200 °C) by PECVD using dichlorosilane (SiH_2Cl_2) and hydrogen (H_2), and we have made a comparative study of cluster density, size, and height, determined by atomic force microscopy (AFM), in order to determine the influence of the substrate on these aspects.

2. EXPERIMENTAL DETAILS

The nc-Si were deposited in a conventional parallel plate RF (13.56 MHz) PECVD reactor using a mixture of SiH_2Cl_2 and H_2. The flow rates, Fr(SiH_2Cl_2) and Fr(H_2), were fixed at 2 sccm and 20 sccm, respectively. A substrate temperature of 200 °C was used in all the cases.

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The RF power density was 0.07 W/cm^2. The electrode distance is 1.5 cm. The deposition parameters were pressure and deposition time. (100) *n*-type single crystalline silicon (c-Si), corning glass, fused silica, and amorphous silicon nitride were used as substrates were used as substrates for the growth of the nc-Si. Prior to deposit, the substrates where carefully cleaned with trichloroethylene and acetone. In the case of silicon, the substrates were also etched in diluted hydrofluoric acid (5% HF). The surface morphology of the samples was studied by atomic force microscopy (AFM) using a Jeol JSPM-4210 on tapping mode and a high resolution Mikromasch NSC15 silicon tip with radius of curvature <10 nm. Measurements of cluster diameter, height and number density were made using the WinSPM, – Process software, Version 407 (.22), © 1989–1999.

3. RESULTS

The time evolution of the early stages of nc-Si growth on the c-Si substrate with a pressure of 350 mTorr is shown by means of the four AFM images of Figure 1. Figure 1(a) shows the AFM image of the nc-Si formed during the first 30 s of growth. The initial growth occurred as flat-topped oval clusters with average diameter of approximately 150 nm. Figure 1(b) shows clusters whose average diameter increases up to 320 nm with one minute of deposit. The clusters coalesce and smaller circular columns begin growing between them at 2 minutes of deposit (Fig. 1(c)). The AFM image after 10 minutes of deposit (Fig. 1(d)) shows a second phase of growth dominated by smaller circular clusters with an average diameter of approximately 85 nm, which have very probably grown over the underlying layer formed by the initial flat islands. The plots shown in Figure 2 compare how the diameter and height of clusters evolve in time for these samples

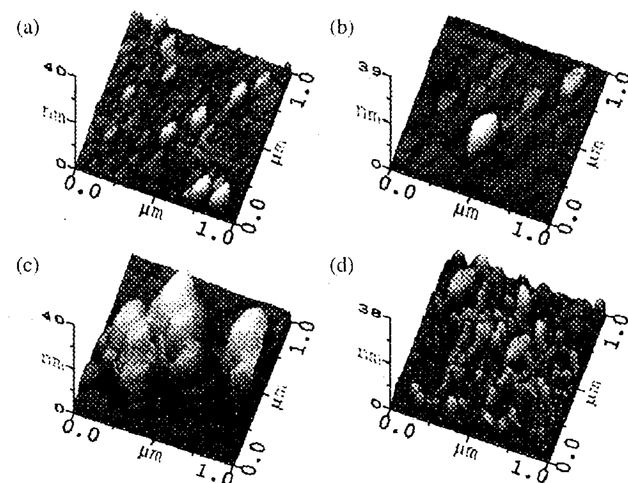

Fig. 1. AFM micrographs showing the early stages of growth of nc-Si deposited at 10 W and 350 mTorr over Si *n*-type substrate with deposition times of (a) 30 s, (b) 60 s, (c) 120 s, and (d) 600 s.

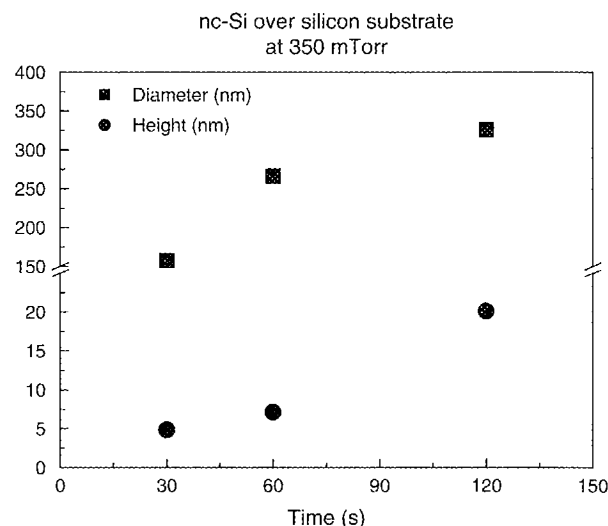

Fig. 2. Plots comparing the evolution in time of nc-Si diameter and height during the first 2 minutes of growth for samples deposited on Si *n*-type substrate at 10 W and 350 mTorr.

during the first two minutes. This evolution indicates that the clusters have preferential growth along the surface or semiepitaxial-type since the increase in diameter is at least one order of magnitude greater than the increase in height.

A comparison between growth over c-Si and corning glass in the first 30 seconds with a pressure of 350 mTorr is shown in Figure 3(a) and (b). These samples were grown simultaneously. Clusters formed on glass have a mean diameter of 35 nm, that is, five times smaller than those formed on the silicon substrate. Also, the mean height of nc-Si grown over glass was of 17 nm although it only reached 4 nm in the case of nc-Si grown onto silicon. On the other hand, the cluster number density increased from 1.57×10^9 clusters/cm^2 on silicon to 1.21×10^{10} clusters/cm^2 on glass. All this indicates that, under these plasma conditions, the columnar growth is favored over glass while growth along the surface is favored over silicon.

To further investigate the influence of the surface chemistry over the shape and size of nc-Si, samples were deposited over (100) *n*-silicon, silica fuse, amorphous silicon nitride and corning glass with a pressure of 500 mTorr for 40 s. The surface morphology of these samples is shown in Figure 4. The particle density over silicon was

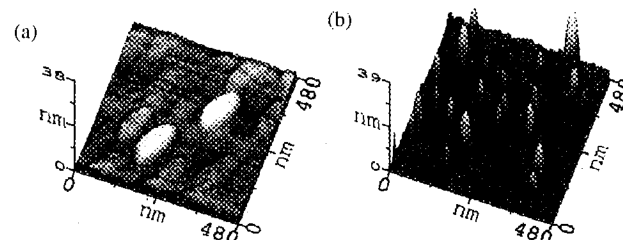

Fig. 3. AFM micrographs of samples deposited simultaneously at 10 W and 350 mTorr for 30 s over (a) Si *n*-type and (b) corning glass substrates.

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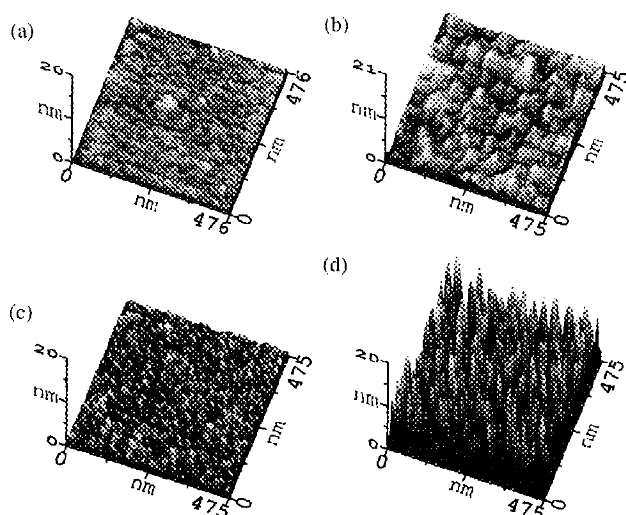

Fig. 4. AFM micrographs showing the influence of the substrate on nc-Si morphology for samples grown at 10 W and 500 mTorr for 40 s over (a) c-Si, (b) silica fuse, (c) a-SiN_x, and (d) corning glass.

1.77×10^{10} clusters/cm^2, but the mean height of the clusters was only 1 nm. It is worth noting that in this case the silicon substrate had a surface mean roughness (R_{av}) without deposit of 0.80 nm while in the deposit zone it decreased to 0.40 nm. We believe that the increase in pressure favored even more the surface growth already observed in Figure 1. On the other hand, clusters grown on fused silica reached a height of 2.3 nm and the number density in this case was 2.48×10^{10} clusters/cm^2. The fused silica substrate without deposit had a very similar mean roughness to the silicon substrate, $R_{av} = 0.90$ nm. In both cases the clusters were extended island type. Clusters formed over silicon nitride ($R_{av} = 1.15$ nm) were circular in shape with a mean height of 2.5 nm. On the glass ($R_{av} = 2.33$ nm) the growth was completely columnar type (mean height of 13 nm). Nevertheless, the particle density on both cases was very similar: 2.2×10^{11} clusters/cm^2 on silicon nitride and 1.88×10^{11} clusters/cm^2 on glass.

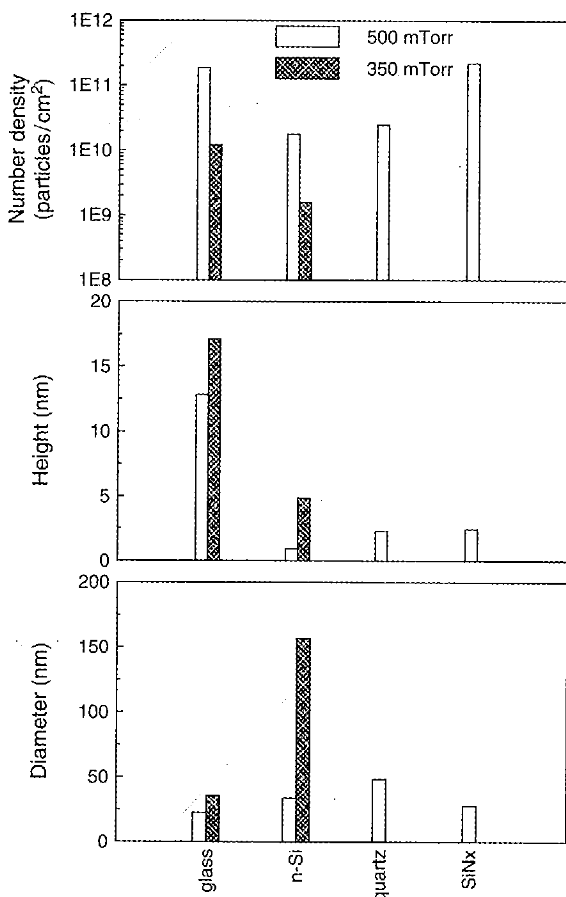

Fig. 5. Plots comparing mean diameter, height, and number density of samples grown over different substrates and with different deposition pressures.

Figure 5 compares the mean diameter, height and number density of all samples described before. The increase of deposition pressure from 350 mTorr to 500 mTorr had the effect of reducing the size of the clusters (both, height and diameter), and of increasing their number density. This effect can be observed clearly when one compares the samples grown over glass at 350 mTorr and 500 mTorr shown in Figures 3(b) and 4(b), respectively. All these results indicate that the surface characteristics influenced importantly the shape, size, and number density of nc-Si.

4. DISCUSSION

We can explain the island growth during the early stages of nucleation in terms of the chlorine chemistry introduced in the PECVD process by means of the use of SiH_2Cl_2 as silicon precursor. As it has been discussed in previous works[12,17] the use of SiH_2Cl_2 favors the predominant incorporation of $SiCl_x$ radicals in the growing film, because the Si–Cl (4.75 eV) bonds are stronger and more stable than the Si–H (3.4 eV) bonds. On the other hand the atomic hydrogen impinging on the growing surface preferentially breaks a Si–Si (2.4 eV) bonds rather than Si–Cl bonds and it creates both, dangling bonds and a Si–H bonds. Hydrogen also can react with $SiCl_x$ gas precursors forming HCl, which results in Cl abstraction. Given the low surface mobility of the Si-Cl_x radicals, these films will be prone to have a columnar and/or isolated islands type structure. Also, as Cl forms terminal bonds, the films are expected to have an open (porous) structure. Given the high chemical affinity between Cl and H atoms to form volatile HCl, the chlorine content in the films can be controlled by promoting the mutual abstraction of Cl and H from the film network during film growth. However, the promotion of these Cl abstraction reactions depends on the deposition conditions. Based on these characteristics, it is well expected to find important differences in the morphology of films deposited at the different pressures used in this work. On the other hand, the chlorinated chemistry of the deposition process favors the formation of clusters with nanometric size within the growing film and even inside the plasma region.[11,17]

Nonetheless, it is clear from our results that surface chemistry also influences greatly in the height, diameter and number density of nc-Si. Each particular substrate has a different chemical affinity with the species formed in the plasma. In the case of silicon substrates, mainly terminated in Si–H bonds and defect-free, most of the surface will be a favorable nucleation site, so semiepitaxial-type growth is expected. For silicon nitride, glass and silica fuse, different terminal bonds are present, such as Si–N, and Si–O and Si–H, respectively. Thus, certain parts of the substrate will be more favorable than others as nucleation sites.

Another factor that influences in the growth kinetics of the film is surface mobility of the different impinging species. Surface roughness could reduce mobility in the case of amorphous substrates, while being negligible for crystalline silicon. Presence of defects on the surface could also favor island growth. This hypothesis is reinforced by the fact that the greatest height was observed on the substrate with higher roughness (glass). Of course, both, surface chemistry and mobility are greatly dependent on deposition parameters as well.

Thus, it is important to take into account that during the early stages of growth of nc-Si (short deposition times or low deposition rates), if a deposit is made over two different substrates the films morphologies are not necessarily the same, even if the samples where simultaneously prepared. Specially, in the case of multilayered structures, nc-Si size and number density in each layer will depend on the surface conditions over which they grow, as well as deposition parameters. Also, one must take into account the influence of the surface chemistry and presence of defects when using different substrates for specific characterization techniques, for example, c-Si for infrared spectroscopy and glass or silica fuse for UV-vis transmission analysis.

5. CONCLUSION

Direct formation of nc-Si over different substrates was demonstrated. This was explained in terms of chlorine chemistry introduced by dichlorosilane precursor. The low sticking probability of $SiCl_xH_y$, Cl and H abstraction reactions and stability of Cl terminal bonds, all favor cluster formation. The influence of substrate surface chemistry, deposition pressure and time on nc-Si diameter, height and number density was studied. Amorphous substrates favor the columnar growth due to different chemical affinities with the impinging species and the presence of surface defects. Clusters formed over glass, amorphous silicon nitride and silica fuse were less than 50 nm in diameter. In the case of (100) n-Si, in which semiepitaxial type growth was favored, cluster size surpassed 150 nm in diameter. Number density of nc-Si was greater on amorphous substrates by at least one order of magnitude. Diameter of nc-Si decreased and number density increased with increasing deposition pressure. It is important to take into account these differences when using different substrates during nc-Si characterization.

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