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Selective Nucleation Based Epitaxy(SENTAXY): A Novel Approach for Thin Film Formation

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We have proposed a novel approach to form the polycrystalline thin films over amorphous substrates, which is named SENTAXY (Selective Nucleation based Epitaxy). The location of the crystalline grains is controlled by manipulating the nucleation sites. The location of the boundaries between the adjacent grains can be also determined by arranging the artificial nucleation sites. The method has been applied to the vapor phase deposition of Si, the solid-state crystallization of amorphous Si films, and the other systems.

1. INTRODUCTION

Thin films deposited over amorphous substrates are amorphous, or polycrystalline at best, due to the lack of the long-range order in the substrate surface. The polycrystalline films consist of the crystalline grains that have various orientations and sizes. The inhomogeneity of the structures could degrade the material qualities in their applications. There have been various attempts to obtain the thin films with some controlled structures, such as graphoepitaxy[1] or diataxy.[2] These methods use the patterned substrate surfaces that align the orientation of the deposited crystalline overlayers. However, they do not control the location of the crystallite nucleation nor of the grain boundaries.

As a novel approach for the highly-tailored thin films, we have proposed a method named SENTAXY (Selective Nucleation based Epitaxy). The method is based on the selective nucleation and growth of a single crystallite at an artificial site. By manipulating such nucleation sites and arranging them spatially, one can obtain a matrix of the uniform crystalline grains in the polycrystalline thin films. In this paper, we present the principle of SENTAXY and its demonstrations in the actual systems. The related issues and the recent progress are also described.

2. PRINCIPLE

The formation of the polycrystalline thin films is initiated by the nucleation of the crystallites. The nucleation occurs at random position and at random time (Fig. 1 (a)), because the nucleation is essentially a probabilistic kinetic process. The nuclei grow to be the crystalline grains and finally impinge on the adjacent grains. This is why the position of the crystalline grains and the location of the grain boundaries are random, and the crystallite size is widely distributed.

The basic idea of SENTAXY is to place the artificial nucleation sites at the predetermined position. The artificial site is not always identical with the real nucleation site, but the small finite area in which the single crystallite selectively nucleates and grows. The probability of the nucleation must be higher in the artificial site than its outside. After the nucleation, the crystallites have to grow beyond the area of the sites. If the nucleation occurs within a period of time which is sufficiently shorter than the whole duration for the growth, and if every crystalline grain grows at nearly the same velocity, the grain size is almost uniform, and the adjacent grains meet near the middle point between their nucleation sites. For instance, if the sites are at the every square lattice point, the grain boundaries make the grid patterns (Fig. 1 (b)). Thus the location of both the grains and their boundaries is controlled.

3. CVD-Si SENTAXY

In the case of crystalline Si films formed by CVD (chemical vapor deposition), the artificial nucleation sites are provided by the difference in the materials of the substrate surface. The final or saturated density of the nuclei is about 100 times higher over Si_3N_4 than SiO_2.[3)-5)] SiO_x (x>2) or SiN_x (x>4/3) formed by CVD or Si-ion implantation are also the materials with the higher density of the nuclei.[6)] If the small portions made of these materials are placed over the SiO_2 surface, they can be the artificial nucleation sites.

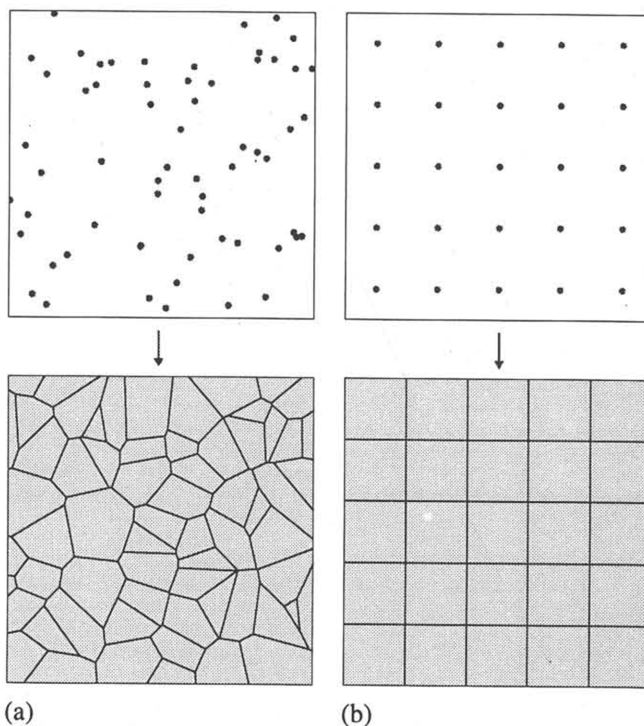

FIG. 1 Schematic representation of the location of the nucleation sites and the resultant crystalline grains. (a) Random nucleation leads to the random boundary location and the broad size distribution. (b) Manipulated nucleation at the square lattice points results in the grid-pattern boundaries and the uniform size distribution.

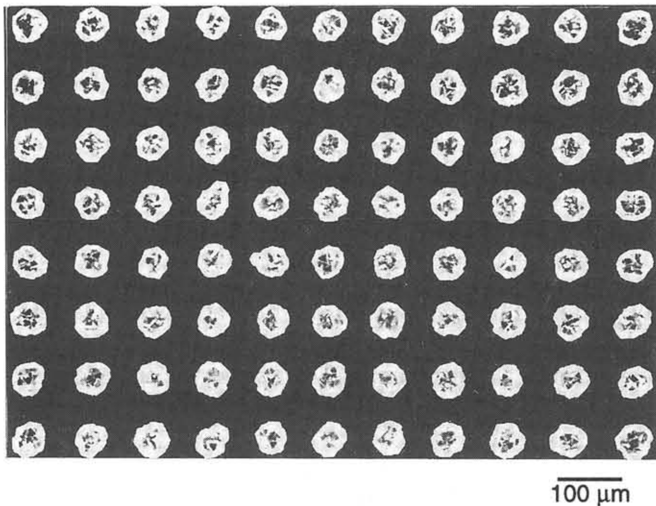

FIG. 2 Plan-view SEM micrograph of the substrate surface of CVD-Si SENTAXY. The artificial nucleation sites of Si_3N_4 (2 μm in diameter) are placed at square lattice points (100 μm in period) over SiO_2. The faceted crystalline grains are grown in matrix.

Figure 2 shows a SEM (scanning electron microscope) micrograph of the typical result. The Si_3N_4 film formed over the thermally oxidized Si wafer was patterned into dots (2 μm in diameter, at each square lattice point in period of 100 μm) with the SiO_2 exposed at the other part. Si was deposited using $SiCl_4$ gas diluted with H_2 gas at 1273 K under 2×10^5 Pa. It is seen in the micrograph that the faceted grains of crystalline Si are set in matrix and they have not impinged on the adjacent grains.

The crystalline grains are classified into three types by their habits. The first type is a part of the single crystal bounded by 8 {111} facets and 24 {311} facets. The second is the simple twin crystal of the first one. The last is the multiply twinned icosahedron bounded by the equivalent {111} facets. The crystalline grains of any type grow like hemispheres. The surface of the as-grown films is not always flat. It is possible, however, to level it by polishing. Moreover, by placing the artificial nucleation sites in the patterned hallows of the SiO_2 substrate, and by selectively polishing the crystalline grains overgrown beyond the hallows, we obtain the discrete islands of the Si crystals. MOSFETs fabricated within such polished grains indicate as good performance as those on the bulk single-crystalline Si wafers.[5]

Only a single crystallite nucleates and grows at an artificial site throughout the deposition using $SiCl_4$ gas.[3] On the other hand, when using SiH_2Cl_2 and HCl simultaneously, the selective nucleation is the more complicated process. We observed a coarsening phenomenon of Si crystallites during the deposition[7],[8] and found that important to make a single crystallite grow at an artificial nucleation site.[9] After some induction period, many submicron-sized crystallites suddenly nucleate within the area of a artificial site. They increase in number but do not grow in size for a while. At a certain time, only one micron-sized crystalline grain immerges among the small crystallites. The large grain rapidly grows, while the others seem to disappear. Finally, the large growing grain occupies the whole area of the artificial site. Such coarsening phenomenon helps the yield of the selective nucleation up.

In the gas condition that the nucleus density is relatively low, it is observed on some artificial sites that the small crystallites entirely disappear although no large grain appears for a long.[8] This observation proves that the small crystallites reevaporate into the deposition atmosphere. It is suggested that HCl, which is an etching agent of Si, plays a crucial role in the reevaporation. The coarsening of Si crystallites is observed not only at the small sites but over the broad area of the same materials. By analyzing the time evolution of the CSD (crystallite size distribution) in detail, it is found that the phenomenon could not be explained by the previously reported mechanisms such as the Ostwald ripening.[7],[8]

4. SOLID-STATE SENTAXY

SENTAXY has been demonstrated also in the solid-state crystallization of the amorphous Si (*a*-Si) thin films that are formed over SiO_2 surface by LPCVD (low pressure chemical vapor deposition).[10]-[12] The nucleation of the crystallites is suppressed by Si-ion implantation into the as-deposited *a*-Si films, which is performed prior to the thermal annealing for the crystallization. The nucleation rate depends on the conditions of the ion implantation. The artificial nucleation sites are provided by forming the two kinds of the areas which differ in the conditions of the ion implantation.

Figure 3 shows a plan-view TEM (transmission electron microscope) micrograph of a typical result. 100 nm-thick *a*-Si films were deposited over thermally oxidized Si wafers using SiH_4 gas under 40 Pa at 823 K. Si^+ ions were implanted uniformly into the as-deposited film at the dose of 4¥10^{14} cm^{-2} and the accelerating energy of 70 keV. Photoresist masks (0.66 μm in diameter) were formed over the *a*-Si film at the square lattice points (3 μm in period). Then the Si^+ ions were implanted again with the masks at the dose of 2¥10^{15} cm^{-2} and the same accelerating energy. The second (local) implantation affects only the unmasked area. The masked areas become the artificial nucleation sites later. After removing the masks, the film was annealed at 873 K in nitrogen ambient. A single crystallite nucleated and grew in each artificial site. The partially crystallized film shown in Fig. 3 has been annealed for 10 h. Dendritic crystallites are seen at the square lattice points in the amorphous background. They have already grown beyond the area of the artificial nucleation site. The selected-area electron diffraction revealed that they were multiply twinned but had the continuous crystalline structures.[13] The film was almost crystallized after 20 h.

The CSDs of SENTAXY show a peak like normal distribution, while those of random nucleation monotonously decreases with size.[10],[11] The random CSDs indicate that the nucleation has been still in the transient state. Based upon the kinetic theory to nucleation, we used the CSDs to measure the nucleation parameters.[14] The steady-state nucleation rate decreases and the time lag for nucleation increases as the accelerating energy or the dose of ions increases, while the growth rate does not change with the ion implantation. The precise control of these parameters was found necessary for the selective nucleation and growth of a single crystallite. By comparing the results of the simulation with the measured dependence, it is suggested that the suppression of the nucleation by the ion implantation originates in the modification of the interface between the *a*-Si film and the SiO_2 underlayer, such as the change of the self-diffusion or of the interfacial energies.[14]

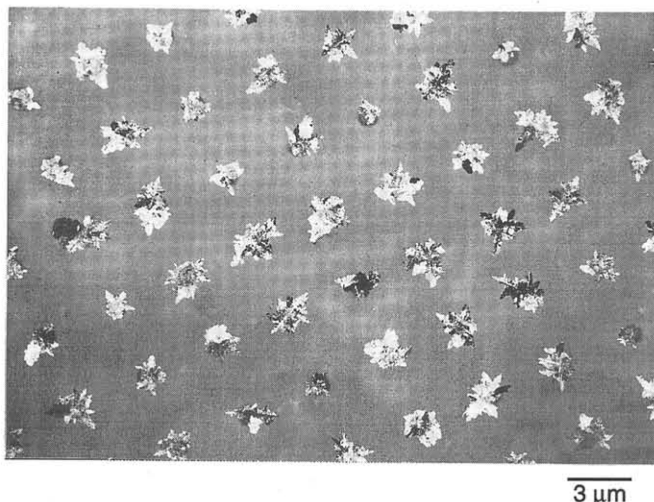

FIG. 3 Plan-view TEM micrograph of a partially-crystallized Si thin film by solid-state SENTAXY. Micron-sized dendritic crystallites are seen at the square lattice points (3 μm in period) in the amorphous background.

Recently, we developed a method to determine the free-energy barrier to nucleation directly from the CSDs independent of any model for nucleation and independent of the barrier to growth, and applied it to the present solid-state system.[15] It is expected that this method is useful to make the suppression mechanism of nucleation clear.

5. SENTAXY IN OTHER SYSTEMS

Noguchi and Ikeda[16),17)] applied the similar approach to the polycrystalline Si (poly-Si) thin films obtained by excimer laser annealing of *a*-Si films. The excimer laser is irradiated onto the *a*-Si film with the patterned overlayer. The patterned overlayer makes the distribution of temperature inhomogeneous. The locally heated portions of the film function as the artificial nucleation sites.

Ma *et al.*[18),19)] deposited diamond films by CVD over the substrate surface with dots of SiO_2 films formed on the Si wafers. The diamond crystallites tends to nucleate over the rough surface, particularly at the edge of the steps. The small dots function as the artificial nucleation sites. Hirabayashi *et al.*[20)] used the substrates on which smooth surface and rough surface coexist. The small portions with the rough surface become the artificial sites.

Tokunaga *et al.*[21)] reported the selective growth of polycrystalline GaAs films deposited by metalorganic CVD. They choose small islands made of the poly-Si films over SiO_2 surface, for the artificial nucleation sites. For the sufficient selectivity, it is necessary to add HCl to the ordinary deposition gas composed of AsH_3, trimethylgallium, and H_2.

Recently, Yang and Atwater[22)] reported an attempt to manipulate nucleation sites in the solid-state crystallization of Ge thin films. They produce arrays of metal dots on top of the amorphous Ge films doped with boron or phosphorous. Through the metal-induced selective-area nucleation,[23)] the metal dots could provide the artificial nucleation sites.

As a related technique, we have also demonstrated a method to place the single seed crystallites formed by agglomerating dots of poly-Si films.[24)] They are epitaxially grown resulting in the similar films of CVD-Si SENTAXY.

6. SUMMARY

We originated a novel approach to the highly-tailored crystalline thin films, which is named SENTAXY, and have demonstrated it. The location of both the crystalline grains and their boundaries is controlled by manipulating the nucleation sites. The application of the principle has been extending among various systems and materials. It is expected that the resulting films provide the materials for the high-performance devices.

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