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Selective Growth of Nuclei on Amorphous Substrates

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A selective-nucleation-based crystal-growth technique over amorphous substrates is demonstrated for the first time. The method named Selective-Nucleation-Epitaxy manipulates nucleation sites and periods and hence, control the grain boundary location by modifing the substrate surface. SiO_2 and Si_3N_4 are used as substrate materials with low and high nucleation density, respectively. Si_3N_4 is patterned into dots, a few μm in diameter, a hundred μm apart over SiO_2. One Si nucleus is selectively formed only in a small area of Si_3N_4. The highly facetted and periodically located nuclei grow over SiO_2 up to ~ 100 μm in diameter without degrading crystallinity. A MOSFET fabricated inside the island operates comparably to the bulk Si control.

INTRODUCTION

Overlayers as-deposited on amorphous substrates are amorphous or, at best, polycrystalline. The absence of long range order in the amorphous substrates is reflected in the absence of long range order in the overlayers. Amorphous films maintain only short range order while polycrystalline films are composed of aggregates of single crystal grains with grain boundaries between adjacent grains. Graphoepitaxy[1-3] introduced the new idea that micro patterning over amorphous substrate surface could alter crystallographic structures in overlayers. In this paper, we propose and demonstrate a novel crystal growth technique named Selective-Nucleation-Epitaxy in which nucleation sites and periods are manipulated by modifing the amorphous substrate surface. This technique enables one to control grain boundary location. It has been considered that nucleation and growth procedures randomly occur and are out of control. This method could be in contrast to epitaxial lateral overgrowth seeded from single crystal substrates[4] and Graphoepitaxy in a sense that this method is based on a phenomenon of selective nucleation which is strongly dependent on amorphous substrate materials.

PRINCIPLE

In general, films are formed over amorphous substrates through nucleation, growth and coalescence. In the early stage of film formation, some adatoms adsorb or desorb on the substrate surface, migrate around and form nuclei. After the nuclei reach a critical size, free energy of the nuclei is lowered and those nuclei readily grow. All such variables that affect nucleation and growth, namely adsorption rate, surface diffusion rate and desorption rate strongly depend on the substrate surface materials as well as growth conditions. In addition, chemical reaction of the adatoms with the surface material is also a dominant factor to determine growth mechanisms. Apparently nucleation density represents above mentioned variables and it is somewhat easily evaluated quantitatively. In an extreme

case, all adatoms desorb, resulting in zero nucleation density and no film formation, although growth environments keep supplying adatoms to the surface.[5] The method which we propose to control nucleation sites and periods over amorphous substrates is depicted in Fig. 1.

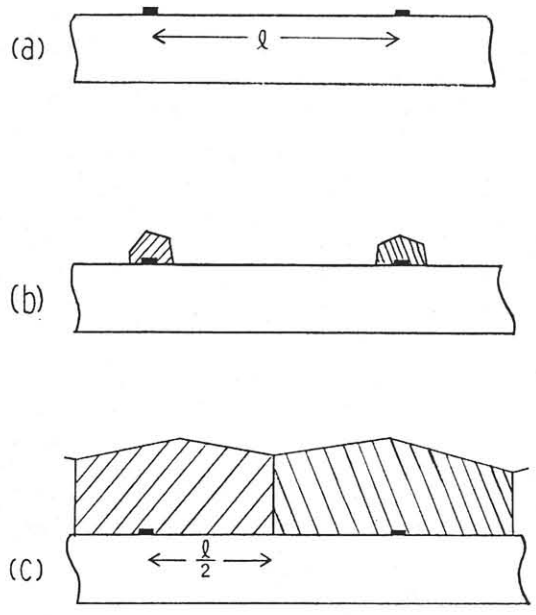


Fig. 1, Depicted principle

A material on which nucleation readily takes place, is placed over a substrate which has extremely low nucleation density, and patterned into a dicrete small area and located in arbitrary periods as shown in Fig.1.(a). When deposition starts on the surface-modified-substrates, only one nucleus is selectively formed in one small area of the higher-nucleation-density-material that is an artifitially arranged nucleation site as shown in Fig.1. (b). The periodically located single-crystal nuclei increase the size and finally grow over the substrate surface without degrading the crystallinity and impinge with adjacent growing islands which nucleated from other sites, resulting in grain boundaries located at the center of the period of the nucleation sites as shown in Fig.1.(c). Therefore, this method enables one to manipulate nucleation sites and periods and hence, grow large single crystal islands in arbitrary size where devices can be fabricated.

EXPERIMENTAL DETAILS

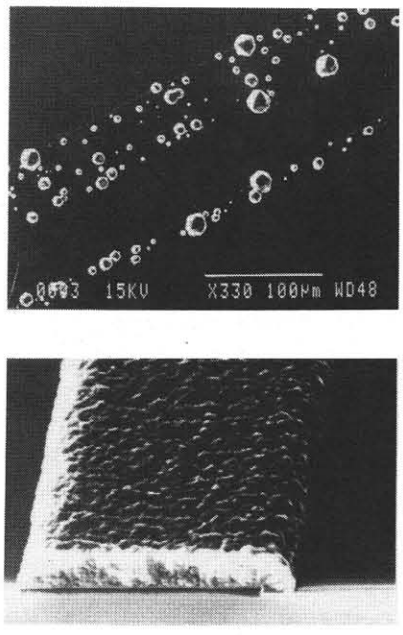
In the case of Si-Selective-Nucleation-Epitaxy, SiO_2 was chosed as a material with low nucleation density. Thermally grown SiO_2 and CVD-SiO_2 were used. Non doped or phosphorus doped SiO_2 was deposited over Si wafers at 400 °C to thicknesses in the range of 0.1 - 0.2 μm. Si_3N_4 was applied as a material with the higher nucleation density which was deposited over or under SiO_2 at 800 °C, 30 nm thick, with SiH_2Cl_2 and NH_3 mixture under 0.3 Torr by LPCVD. The Si_3N_4 was patterned into dots, 1.2, 2.0 and 4.0 μm in diameter, 50, 100, 200 μm in period using photolithography and reactive ion etching with SF_6. Some Si_3N_4 films are patterned into stripes, 10 μm and 50 μm in width. After careful cleaning of the substrates, Si was grown at temperatures in the range of 700 °C - 1150 °C under pressures in the range of 760 - 150 Torr by a CVD epitaxial reactor with $SiCl_4$ or SiH_2Cl_2 diluted with H_2. In some cases, HCl additional gas was introduced. In order to measure the nucleation density and observe growth morphology, an optical microscope and a field emission type scanning electron microscope (FE-SEM) were used. A micro area X-ray diffraction with tightly focused X-ray beam, ~ 30 μm in diameter, cross-sectional transmission electron microscope (XTEM) and defect delineation etching were applied to study structural properties. C-V and Hall measurements and fabrications of PN diodes and poly-Si gate P-channel MOSFETs were carried out to evaluate electrical characteristics.

RESULTS AND DISCUSSION

Si nucleation densities over Si_3N_4 and SiO_2 were found to be a strong function of growth temperatures in a gas system of $SiCl_4$ and H_2 and they were proportional to inverse of temperature. Other growth conditions such as pressure and flow rates of source gases also affected. Nucleation densities were saturated immediately and the difference between on SiO_2 and Si_3N_4 was 10^2 - 10^3 cm^{-2}. Nucleation densities over other materials in other gas systems,which expand the difference , will be reported elsewhere. In order to demonstrate selective deposition over amorphous substrates, two typical stages of nucleation and film formation are shown in Fig. 2.

(a)
0.8 min.

(b)
20 min.



1 µm

Fig. 2, Selective deposition on stripes

Si was deposited on the substrate where Si_3N_4 thin film was patterned into stripes over SiO_2 by reduced pressure CVD with $SiCl_4$ diluted by H_2 at 150 Torr and 1000 °C. Those conditions provide nucleation densities of 10^3 and 10^6 cm^{-2} for SiO_2 and Si_3N_4 respectively. Si nucleates only on Si_3N_4, not on SiO_2 in 0.8 minute as shown in Fig.2.(a) and a 6 µm-thick polycrystalline Si continuous film is formed in 20 minutes on Si_3N_4 as shown in Fig.2.(b). X-ray diffraction revealed that the Si film had a strong (110) texture and was composed of grains ~0.5 µm in diameter. Selective growth of nuclei on a small area of Si_3N_4 over SiO_2 substrates was carried out by the same experimental conditions as in selective depositon on stripes shown in Fig. 2. Procedures to form one Si nucleus selectively in a small patterned Si_3N_4 are shown in Fig.3.(a)-(c).

(a)

(b)

(c)

1 µm

Fig.3, FE-SEM micrographs of Selective-Nucleation-Epitaxy

The micrograph in Fig.3.(a) gives the substrate surface morphology where Si_3N_4 appears in a window of SiO_2, 2 µm in dia-

meter. Si_3N_4 surface is somewhat rough rather than SiO_2, presumably due to reactive ion etching. Onset of Si nucleation on the substrate is shown in Fig.3.(b). A highly facetted single nucleus is selectively grown at the center of the window. Further deposition increases the nucleus size which fully covers the window and lateral overgrowth starts on SiO_2 as shown in Fig.3.(c). On this initial nucleation stage, the smaller nucleation site i.e. Si_3N_4 area tends to select one single nucleus which strongly affects crystallinity in growing islands. For example, growing large islands, which nucleated from the sites of 4 μm in diameter, are highly defected or, at worst, polycrystalline. When the growth continues, the highly facetted and periodically located sigle nuclei increase their size laterally over SiO_2 and finally impinge with adjacent islands, resulting in distinct grain boundaries which are clearly located at the center of nucleation sites' period. It was confirmed by cross sectional SEM combined with defect delineation etching and XTEM. The islands successfully grew up to ~100 μm in diameter, without degrading crystallinity. Initial nuclei less than the nucleation sites are found to be single-crystalline or twin or multiple-twinning-particles by SEM observation of the equilibrium forms. However, highly facetted growing islands larger than a few tens μm in diameter are singlecrystalline as long as we judged from micro area X-ray diffraction and XTEM although defects like stacking faults are localized near the interface between Si and the substrates. XTEM shows that the defects reduce dramatically toward the surface of the islands. After planarizing the large islands by lapping and polishing, a P-channel MOSFET has been fabricated inside an island and hole mobility of 180 (cm^2/v.sec.) with leakage current less than 10^{-12} (A/μm) which is almost identical with the bulk Si control. Details of crystallographic and electrical properties will be reported elsewhere.

CONCLUSIONS

We demonstrated a novel crystal growth technique of Selective-Nucleation-Epitaxy which enables one to manipulate nucleation sites and periods over amorphous substrates. In the case of Si, Si_3N_4 is patterned over SiO_2 substrate surface and Si is deposited over the surface-modified-substrate by CVD. Only one Si nucleus is formed in one Si_3N_4 area, a few μm in diameter, and successfully grown up to ~100 μm over SiO_2. Distinct grain boundaries are artifitially located at the center of the period between the nucleation sites. Growing large islands are single-crystalline and a MOSFET fabricated inside an island is comparably operated to the bulk Si control.

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