Investigation on Preparation of Ge Quantum Dots in SiO_2 Thin Films

Chen Jing, Wu Xuemei, Jin Zongming, and Yao Weiguo
(Physics Department of Suzhou University, Suzhou, 215006, China)
(National Lab for Infrared Phys., CAS, Shanghai, 200083, China)

Abstract

Ge quantum dots in SiO_2 thin films were prepared by r.f. magnetron co-sputtering using a Ge, SiO_2 composite target. The size of quantum dots was modulated by controlling of substrate temperature during depositing and annealing of samples deposited at certain substrate temperature. A series of work was done on the influence of preparing parameters on the growth of quantum dots, and a discussion on the formation and growth of quantum dots under different preparation parameters is given.

1. Introduction

Comparing with the bulk semiconductor crystal, the semiconductor microcrystallites, which are embedded in insulating matrix and small compared to bulk exciton Bohr radius, exhibit three-dimensional electron and hole confinement from which they show discret, large-molecule-like electronic states that shift to high energy with smaller particle size. SiO_2 thin films embedded with semiconductor microcrystalittes, commonly referred as quantum dots, have attracted considerable interest in the fields of solid state physics and material science, because of the potential of these material for optical device applications due to their nonlinear optical properties[1-4]. The establishment of a thin film preparation technology is indispensable for the study and the preparation of high quality films. In this paper, we report the preparation technology of Ge quantum dots embedded in SiO_2 thin films by used of r.f magnetron co-sputtering technique. A series of work has been done on the influence of preparation parameters on the growth of quantum dots, and a discussion on the formation and growth of quantum dots under different preparation parameters is given.

2. Experiment detail

SiO_2 thin films embedded with Ge quantum dots, which were about 500nm in thickness, were prepared by r.f. magnetron co-sputtering technique in an Argon presure of 3.5 Pa from a Ge, SiO_2 composite target on substrate of Si(100) and optical quartz glass according to the subsequent requirement. Substrate cleaning included degreasing using successive rinses in acetone, alcohol, and deioned water followed by dry treatment.

The target is composed of two disks of ϕ50mm. The back disk is a high purity Ge single crystal (3mm in thickness), and the frontal disk is a piece of 99.99% purity SiO_2 with three holes on it. In order to obtain different content of Ge in the film, we have several SiO_2 disks with different size of hole on it with which we can get different relative surface area of Ge. The size of Ge quantum dots is modulated by the controlling of substrate temperature (Ts) during depositing and the temperature of afterward annealing (Ta) of samples deposited under certain substrate temperature, respectively.

X-ray diffraction (XRD, D/max-IIIc) analysis of the films were performed from 20° ~ 60° (2θ). The average size of particles was evaluated using the Scherrer's formula, in order to study the influence of preparation parameters on the size of Ge quantum dots.

3. Results and discussion

3.1 The influence of deposition parameters on the growth of Ge crystal during depositing

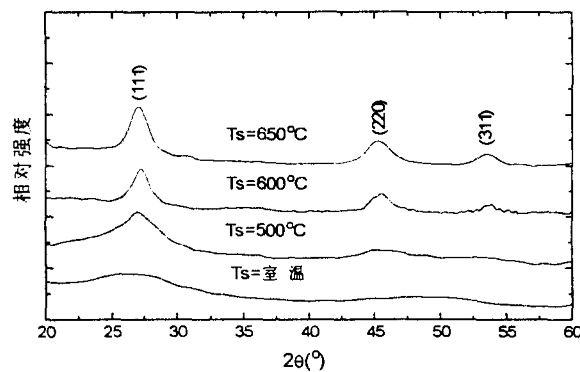

Fig. 1 XRD patterns of samples prepared under different Ts (P = 300w)

Fig. 1 shows the XRD spectra of films deposited at Ts of room temperature (RT), 500℃, 600℃, and 650℃, respectively. For Ts = RT, the spectrum shows that there is only amorphous structure in the films. For Ts = 500℃, the crystal peak appears, it means that there exist Ge microcrystallites in the films. As the Ts increasing further, the spectrum (Ts = 600℃) shows that there are three peaks in the region of 2θ =20° ~ 60° which are denoted as (111), (220), and (311) of diamond structure, respectively. The up'most spectrum in Fig. 1 shows same as the spectrum of Ts = 600℃ with the narrower peak widths which means that the crystal size is larger. The results of XRD indicate that at low Ts there only exists amorphous structure of Ge in the as-deposited films, as Ts increasing to a certain degree (about 500℃) the Ge microcrystallites come to exist, and the crystal size of Ge becomes larger with the higher Ts.

In order to optimize the preparation condition, the influence of sputtering power (P) on the growth of Ge crystal has been studied. As shown in Fig.2, the crystal size of Ge

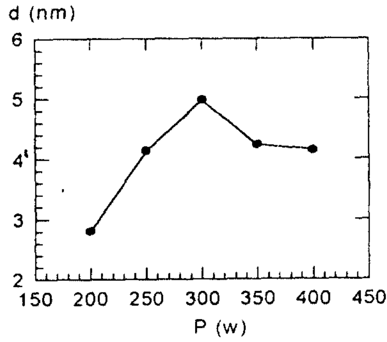

Fig 2 Dependence of d on P
(Ts=600°C, t=45min)

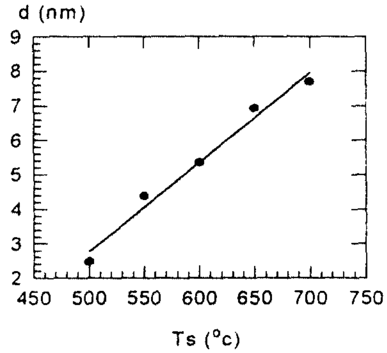

Fig 3 Dependence of d on Ts
(P=300w, t=45min)

increases with the increase of P at low power, but it does not increase monotonously with the increase of P. There is of a peak at about 300w. Fig.3 shows the dependence of d on Ts at the optimized sputtering power of 300w, from which we can see that the crystal size of Ge increases almost linearly with the Ts in the range of 500~700℃ at the optimized power. It means that the crystal size of Ge can be controlled effectively by the Ts during depositing.

3.2 The influence of annealing technology on the growth of Ge crystal

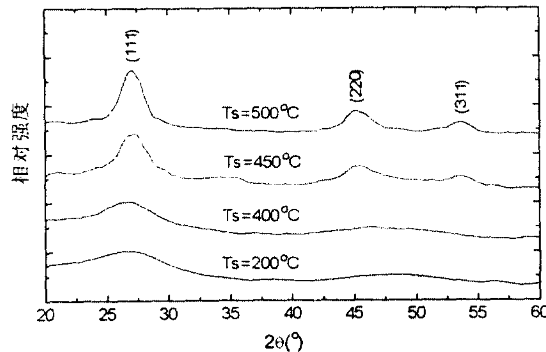

Fig 4 XRD patterns of samples prepared at different Ts with same annealing condition
(Ta=650°C, t=2h)

Experiment results how that the size of Ge crystal can be controlled by Ta and annealing time, respectively, and attention should be paid to the Ts. As shown in Fig.4 after annealing of films prepared at low Ts(<450℃), there is no Ge crystal can be detected by XRD. It means that, for samples deposited at low Ts, it is difficult to form the crystal in the annealing time of 2h at Ta=650℃. At Ts=500℃, the dependence of d on Ta is shown in Fig.5, from which d increases with the increase of Ta, but in the range of Ta = 500~700℃ the increase of the size is not much as that mentioned above (Fig.3).

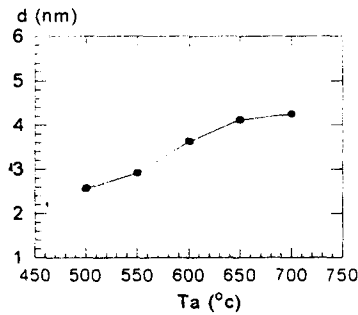

Fig 5 Dependence of d on Ta (Ts=500°C, P=300w, t=2h)

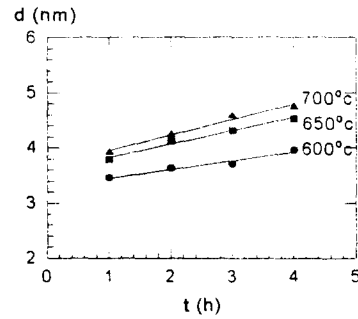

Fig 6 Dependence of d on annealing time (Ts=500°C, P=300w)

As we know with longer annealing time the size of Ge crystal will be larger, Fin.6 gives the results of dependence of d on the annealing time at different Ta. As shown in Fig.6, the size of Ge crystal is larger with the longer annealing time, but the modulating range of size of Ge crystal is only about one nanometer in the annealing time of 4 hours.

As we know, the surface migration of atoms is the base of the nucleation and growth of thin films during depositing. For the deposition of composite films, the surface migration and precipitation of Ge particles must be considered. At low Ts, due to the deposited atoms have insufficient energy of migration to form clusters, and due to the requirement of certain energy to transfer clusters to microcrystallites, so it is difficult to form Ge crystal even if the clusters have formed with plenty of atoms in it. There must be an energy barrier for the formation of Ge crystal. It is obvious that the size of Ge crystals in the composite films can be effectively controlled by Ts which should be higher than that of the energy barrier.

It is well known that there exist two diffusion models for the two technologies. For the controlling Ts during depositing atoms diffuse mainly on the surface during depositing, and for afterward annealing of samples atoms diffuse in the body. The diffusion rate on the surface is larger than that in the body, so the formation of the Ge crystals will be easy and the growth of Ge crystals will be fast by the controlling of Ts during depositing. For the afterward annealing of samples, the growth of crystal size is slow as shown in Fig. 6, and with the longer annealing time and the higher Ts, the crystal size will be larger.

4. Conclusion

In summary, the composite films of Ge microcrystallites embedded in SiO_2 thin films were prepared by r.f. magnetron co-sputtering technique using a Ge, SiO_2 composite target. The growth of Ge crystals was studied by controlling the Ts during depositing and afterward annealing of samples, respectively. Results show that the

growth of Ge crystals was controlled effectively by the both methods, but the features of the growth of Ge crystals are differ from each other caused by the different diffusion model.

References

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