Initial Molecular Beam Epitaxial Growth of ZnSe on Si Substrates

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Abstract

Reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), and Auger spectroscopy (AES) were used to study the initial stages of growth of ZnSe on Si substrates by molecular beam epitaxy. We made a comparison of the ZnSe growth on Si substrates with different crystal orientations: (111), (110), (211), (100) and (100) misoriented 4°. We found that the growth mode strongly depends on the substrate orientation, the formation of islands is more clearly observed for the (111) substrate. This could be caused by the particular surface energy and bonding conditions on the (111) orientation. The island formation at the initial stage of growth on Si(111) could be used to synthesize self assembling ZnSe-quantum dots.

1. Introduction

Currently ZnSe is one of the most interesting materials aiming to the development of light emitting optical devices in the blue-green color [1]. Laser diodes have been fabricated with ZnSe based materials grown over GaAs substrates due to the similarity in their lattice constants (~0.26 % lattice mismatch). However the growth of ZnSe on Silicon surfaces is very attractive considering the possibility to integrate the optoelectronic properties of ZnSe with the advanced Si-technology. In fact Si is a unique substrate due to its exceptional perfection, purity, low cost, and its better mechanical and thermal properties compared with those of GaAs.

In this work we report on the initial stages of the molecular beam epitaxial (MBE) growth of ZnSe on Si substrates analyzed by reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), and Auger spectroscopy (AES). We made a comparison of the ZnSe-growth on (111)-, (110)-, (211)-, (100)-, and (100) 4°-misoriented Si substrates. With the aid of the RHEED patterns we obtained qualitatively the lattice constant relaxation in the system ZnSe/Si(111).

2. Experimental

Typically the oxide desorption temperature of Si substrates in vacuum is 1100°C or higher. Thus, in order to low the desorption temperature, all the Si substrates were prepared employing the method described by Ishizaka and Shiraki [2]. After the chemical treatment, the substrates were mounted on indium-free molybdenum blocks, and then introduced in a 32P-Riber MBE system. In order to evaporate some volatile contaminants like water and alcohols the next step was a degas-procedure raising the substrate temperature up to ≈320°C for 30 min. Then in the growth chamber in order to remove the thin oxide layer the substrates were heated at 780 °C for 10 min. Solid sources of Zn and Se were used with a beam equivalent pressures of 1×10^{-6} and 2×10^{-6} Torr, respectively. At a substrate temperature of 230°C the Si substrates were exposed for 1 min. to the Zn-beam (with the Se-shutter closed). Then we grew ZnSe using a cycled deposition process, one cycle of this process consisted in the next steps: Se-shutter opened for 5 sec. with the Zn-shutter closed; next to this we closed the Se-shutter and opened the Zn-shutter for 5 sec. We expect to grow one monolayer (ML) of ZnSe in each one of these cycles. We grew samples with 3, 7, 15, and 30 cycles of ZnSe on Si (111) substrates with the intention of analyzing in detail the initial growth process on this orientation. In addition for comparison purposes, 7 cycles of ZnSe-deposition were performed on (110)-, (211)-, (100)-, and (100) 4°-misoriented Si substrates. During the growth we *in-situ* monitored the RHEED patterns which were tape-recordered for a subsequent analysis. Before and after the growth, without breaking the UHV conditions, the samples were analyzed by Auger spectroscopy in an analysis chamber connected to the MBE chamber by an UHV tunnel. Finally AFM surface images were taken in air immediately after they were removed from the MBE system.

3. Results and Discussion

Figure 1(a) shows the RHEED pattern of a Si(111) substrate observed along the $[1\bar{1}0]$ direction after the desorption process at 780°C during 10 min. The 7×7 surface reconstruction is clearly observed indicating a substrate surface free of contaminants. This is supported by AES measurements in which we found no traces of oxygen nor carbon. After the Zn-exposition for 1 min. at 280°C the RHEED pattern did not change the 7×7 surface reconstruction was not modified. Moreover, Auger measurements after the Zn-exposure showed no traces of Zn, which could be due to the small sticking coefficient of Zn to Si [3]. However during the first cycle, when the Se-

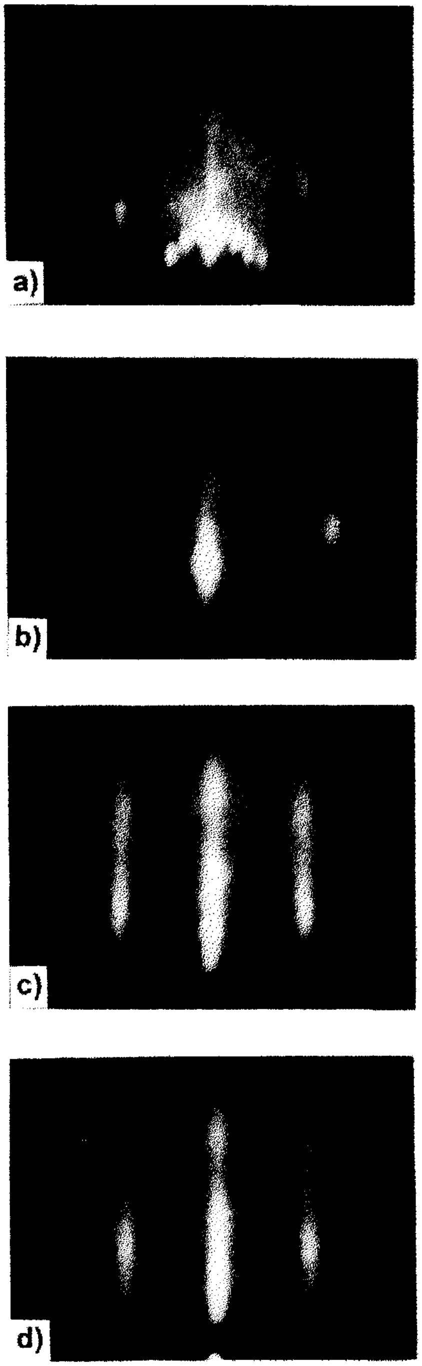

Fig. 1. Evolution of RHEED patterns during the growth of ZnSe on Si(111). a) RHEED pattern from the clean Si(111) substrate. b), c), and d) are the RHEED patterns observed after 3, 15 and 30 cycles of ZnSe growth

shutter was opened the reconstruction was lost significantly, and the pattern became rather diffuse suggesting the formation of a $SiSe_x$ layer due to the high reactivity of Si and Se [4]. Then when the Zn-shutter was opened again (Se-shutter closed), the RHEED pattern became spotty indicating that the first deposited ML grew in a three-dimensional mode. Figure 1(b) shows the spotty RHEED pattern obtained after 3 ML of ZnSe deposition. The inferred three dimensional growth mode is confirmed by the AFM image shown in Fig 2(a), where the formation of islands can be clearly observed. For 7 cycles of ZnSe deposition the RHEED pattern was practically the same of Fig. 1(b), however the island density increased to about 20 islands per μm^2, as we can see in Fig 2(b). These islands have a diameter of ~600 Å with a height of ~20 Å. Similar islands have been obtained by others authors in other different systems, for example: InGaAs on GaAs [5], InP on InGaP [6], Ge on Si [7], and very recently when growing CdSe on ZnSe [8]. The origin of island formation is not clear, but there is a consensus that one of the principal factors is the strain energy due to the lattice mismatch between the epilayer and the substrate [9]. In the case of ZnSe on Si this mismatch is about of 4%.

The island formation in strained heteroepitaxial systems is currently attracting much attention due to the possibility of synthesizing self-assembling quantum dots [5-9]. These zero-dimensional quantum systems have been realized principally in III-V compounds [10,11], however recently the formation of self-assembling CdSe quantum dots was reported [8-12]. With an appropriate control of the island formation in our experiments we could synthesize ZnSe self-assembling quantum dots on Si(111) substrates.

At about 10 cycles of ZnSe deposition the spotty RHEED pattern became streaky. In Fig. 1(c) we show the streaky RHEED pattern for 15 cycles of deposition, from its corresponding AFM image shown Fig. 2(c) we can also see that the three-dimensional growth mode is disappearing, the surface rms roughness of this surface is 2 Å. This is more evident in the RHEED pattern and AFM image for a deposition of 30 cycles, shown in Figs. 1(d) and 2(d), respectively. In Fig. 2(d) we can see only slight traces of the islands, the area between islands has been considerable smoothed out and the surface rms roughness

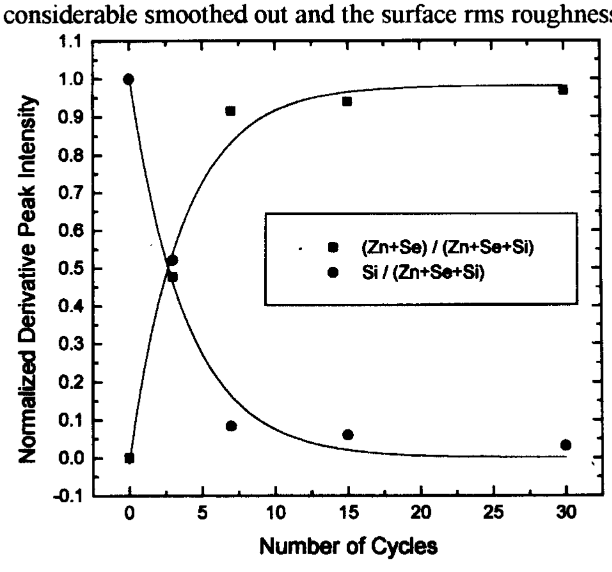

Fig. 3. AES derivative peak intensity as a function of the number of deposition cycles of ZnSe on Si(111).

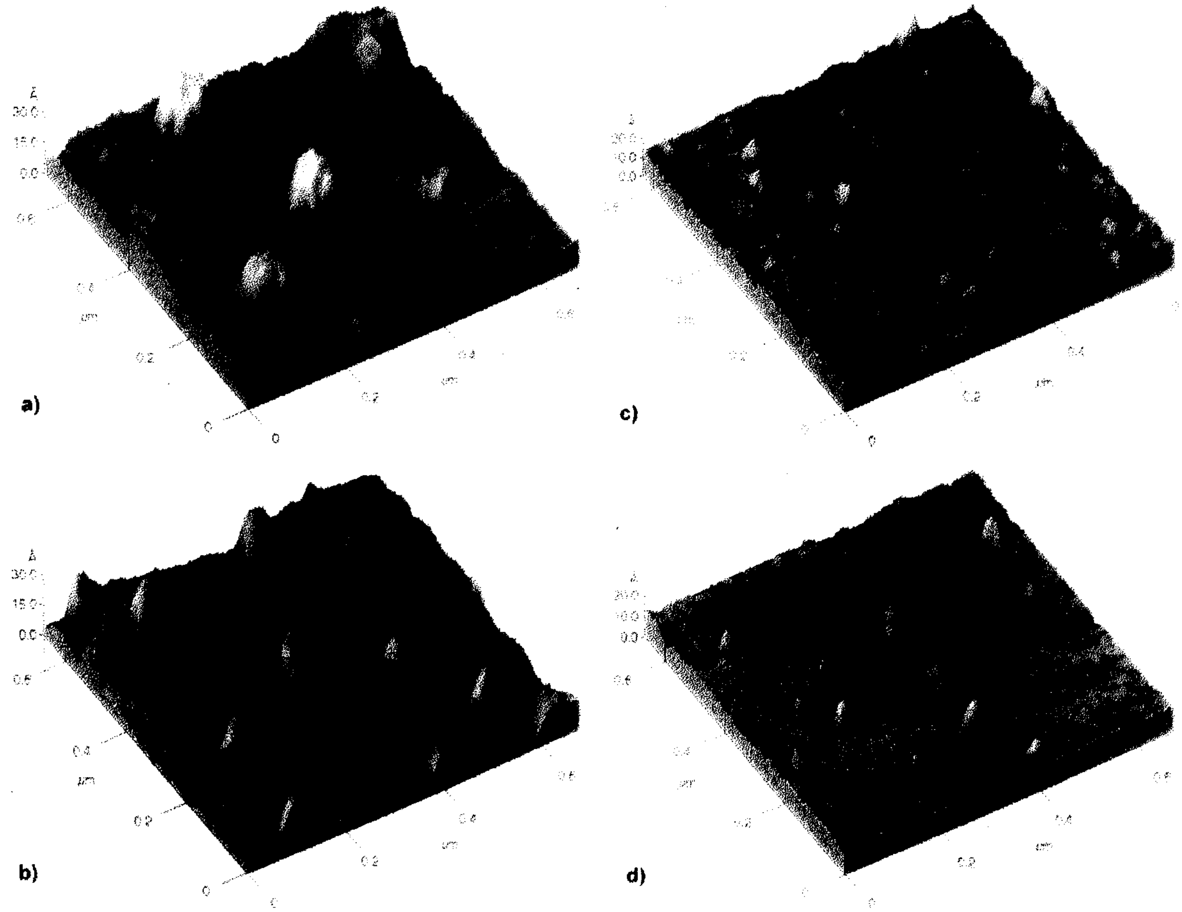

Fig. 2. AFM images of the surface after the growth of a) 3, b) 7, c) 15, and d) 30 cycles of ZnSe on Si(111).

decreased to 1.5 Å, however some tips of the highest islands are still observed. In Fig. 3 we have plotted the variation of Zn+Se and Si Auger derivative peak intensity as a function of the deposition cycles. From this figure we can observe that for 15 and 30 cycles of deposition the substrate has been considerably covered by the epilayer, this in accordance with the RHEED results where at about 10 cycles of deposition we recovered the streaky patterns.

We obtained information of the ZnSe lattice relaxation for the growth on Si(111) by monitoring the RHEED spots spacing during the deposition process [13]. In Fig. 4 we show the change in the ZnSe lattice constant as a function of the number of cycles. From this figure we can clearly see that from the 10^{th} cycle the lattice constant of the epilayer begins to increase. In the 14^{th} cycle we have practically the relaxed ZnSe lattice constant. Therefore we find that the critical thickness of ZnSe on Si(111) is around 10 ML.

It is important to note the big difference in the growth mechanism of ZnSe on Si(111) compared to that on other substrate orientations. In Fig. 6 we show the AFM images for the growth of 7 ML of ZnSe on (100)-,

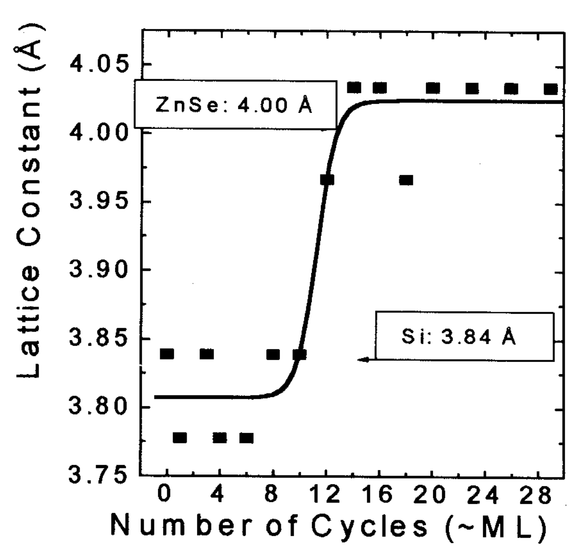

Fig. 4. Lattice constant relaxation of ZnSe on Si(111) in the direction $[1\bar{1}0]$.

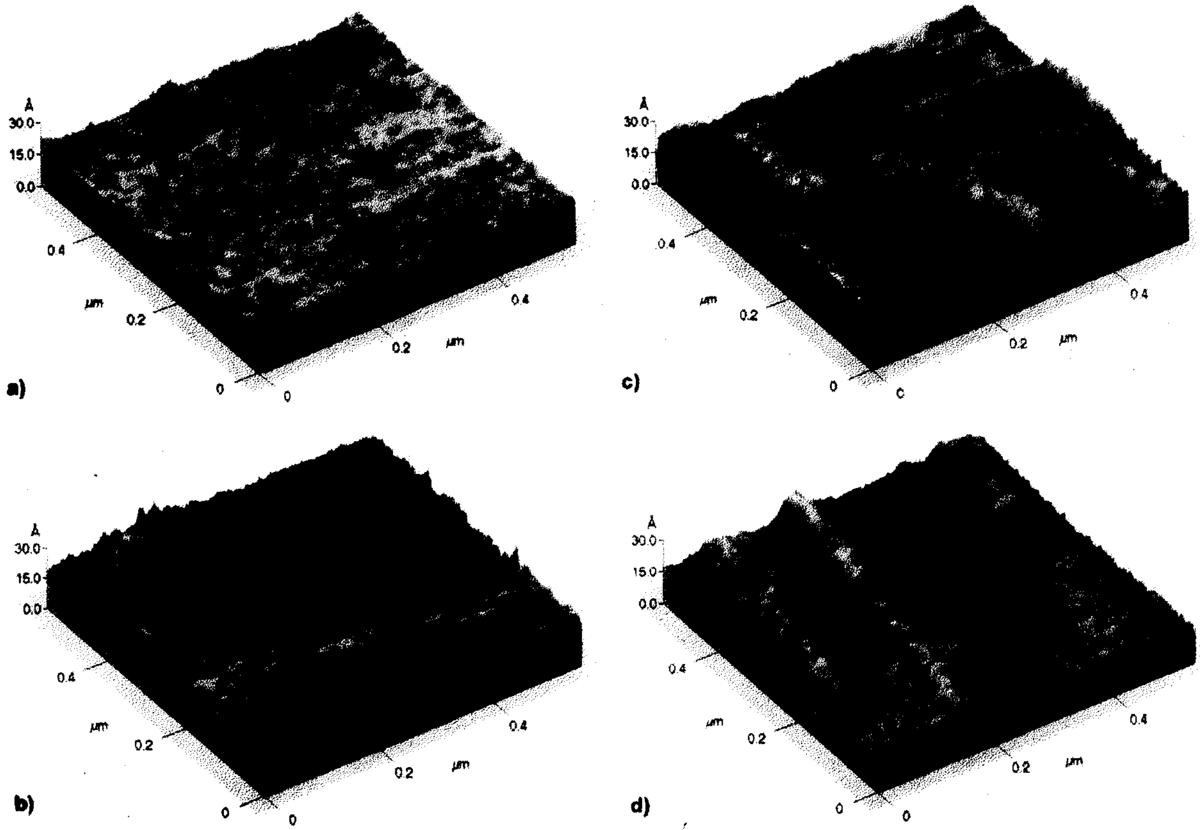

Fig. 5. AFM images of the surface after the growth of 7 cycles of ZnSe on: a) Si(100), b) Si(100) misoriented 4°, c) Si(110), and d) Si(211).

(100) 4° misoriented-, (110)-, and (211)- Si substrates using the same alternated deposition process. We observed that the growth mode strongly depends on the substrate orientation, the formation of islands is more clearly observed for the (111) substrate (Fig. 2(b)). Therefore, the island formation should be caused by the particular surface energy and bonding conditions on the (111) orientation. For example, in the homoepitaxial growth of GaAs it has been reported that the (111) orientation promotes the formation of hillocks which are not observed on other orientations [14].

In summary, we have studied the initial growth process of ZnSe on Si substrates. On Si(111), ZnSe grows in a three dimensional mode forming islands at first stages of the deposition. After 7 cycles of deposition the islands height is ~20 Å with a diameter of ~650 Å, and a density of ~20 islands per μm^2. An appropriate control of the shape and density of the islands could be advantageous to synthesize ZnSe self-assembling quantum dots. The critical thickness using this alternated deposition procedure was estimated to be ~10 ML. A change to a flat surface was observed at around 30 cycles of deposition. The growths on other substrate orientations permitted us to conclude that the island formation is a peculiar characteristic of the (111) orientation.

Acknowledgments
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