

ZnSe epitaxial films grown by MBE on nitrogen treated Si(111) substrates

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Abstract

We have prepared ZnSe epilayers by pulsed molecular beam epitaxy (MBE) on Si(111) substrates, irradiated with a plasma of nitrogen (N-plasma) prior to the deposition. These samples were compared with ZnSe epilayers prepared by conventional MBE directly on untreated Si substrates. The reflection high-energy electron diffraction (RHEED) patterns during the pulsed MBE growth on the N-plasma treated Si surface showed very well defined streaks, and a two-fold reconstruction was observed indicating an atomically flat surface. In sharp contrast spotty RHEED patterns with a diffuse background were observed during the initial stages of the conventional MBE growth, indicating an initial three-dimensional growth mode. A strong evidence of the improved epitaxy, and the two-dimensional nucleation obtained with the use of N-plasma Si substrate surface treatment was the clear presence of large amplitude RHEED oscillations. Auger measurements revealed a better ZnSe-coverage of the substrate for the N-plasma treated Si surface, supporting the idea of a layer by layer growth promotion by this technique. AFM images confirmed a flatter ZnSe surface for this sample.

1. Introduction

The growth of ZnSe epitaxial films on Si substrates is very attractive considering their technological applications, such as the possibility of monolithic integration of ZnSe optical devices with Si electrical devices. Recently ZnSe/Si based devices like; electroluminescent cells[1], photoelectric cells[2], and visible-sensitivity emitter bipolar transistors[3] have been demonstrated. However the performance of such devices is limited by the poor crystal quality of ZnSe epitaxial films on Si[4].

High quality ZnSe epilayers are difficult to obtain due to the chemical and mechanical mismatch between ZnSe and Si. The ~4.3% lattice mismatch and the difference in the thermal expansion coefficients between these two materials are responsible for the introduction of crystal defects like dislocations and stacking faults[5,6]. On the other hand, it is known that an imbalance in the interface charge is one of the serious problems associated to the growth of a polar semiconductor on a nonpolar one[7]. For example, at the (100) interface between Si and the Se plane of ZnSe, the interface bonds will each receive a total of 5/2 electrons per bond instead of the two electrons required[8]. This excess charge would generate a huge internal electric field. Harrison et al[7] suggested that in order to eliminate the excess charge the growth process itself produces modifications in the ideal atom arrangement resulting in a distorted interfacial geometry. Moreover, the bonding problems at the interface are such that in the absence of any flux of Se the sticking coefficient of Zn on the Si surface is very small[4]. Furthermore, chemical reactions between Si and Se at the interface during the very initial stage of growth cause the formation of a thin $SiSe_X$ amorphous interlayer[9,10]. This layer hinders the smooth growth of ZnSe, resulting in a high density of crystal defects in the films. From the above stated problems is clear that the control of the initial stages of growth is essential in order to reduce the defect density.

In this paper we describe the effects of Si substrate surface irradiation with a plasma of nitrogen (N-plasma) prior to the molecular beam epitaxial (MBE) growth of ZnSe. We found that a substantial improvement on the crystal quality of ZnSe epilayers on Si(111) can be achieved by this novel substrate surface treatment with N-plasma. The use of this surface treatment allowed us to obtain a two dimensional growth of ZnSe on Si, as revealed by the presence of reflection high-energy electron diffraction (RHEED) oscillations at the initial stages of growth.

2. Experimental

N-type Si(111) substrates were used in this work. They were degreased and etched to produce a thin protective oxide layer employing the method developed by Ishizaka and Shiraki[11]. Immediately after this process the substrates were mounted on In-free molybdenum blocks, and loaded into a Riber 32P MBE system. The substrates were outgassed at 250°C for 10 min in the preparation chamber with a base pressure of $\sim 8\times10^{-11}$ Torr, and then introduced into the MBE growth chamber. By heating the substrates at ~800°C for 10 min the thin oxide layer was desorbed. After this thermal cleaning process a clear (7×7) RHEED pattern typical of a clean Si(111) surface was observed as shown in Fig. 1(a). Then the substrates were subjected to the surface treatment with N-plasma, which will be described in the next section. The growths were carried out by using elemental cells of Zn and Se with flux pressures of 1×10^{-6} and 2×10^{-6} Torr respectively. We used a pulsed MBE growth mode[12] in which the Se- and Zn-shutters were alternately opened for 2 sec, respectively.

Epilayers grown by conventional MBE (both shutters opened simultaneously) directly on untreated Si substrates were also prepared for comparison purposes. All the growths were initiated by 1 min exposure to the Zn flux. RHEED patterns along the $[1\bar{1}0]$ azimuth were observed during the growth, they were recorded using a CCD camera and a video tape recorder system. The intensity of the RHEED specular spot during the growth was measured by placing a photodiode in front of a TV monitor at the position of the specular diffraction spot. The samples were transferred in vacuum to an analysis chamber to perform Auger measurements. After the growth the samples surface was analyzed in air by atomic force microscopy (AFM).

3. N-plasma Si surface treatment.

Once that the oxide desorbtion has been completed (~800 ^{o}C), the substrate temperature was lowered down to ~600 °C. Then N_2 gas was introduced in the MBE chamber through a precision leak valve, maintaining the background pressure at about 2×10^{-7} Torr. In order to increase the reactivity of nitrogen with the Si surface, an rf-plasma discharge source (Oxford Applied Research) operated at 380 W was used to produce highly reactive nitrogen species[13]. The Si surface was exposed to the N-plasma for 10 min, then the substrate temperature was lowered under the N-plasma to avoid possible loss of nitrogen bonded to the Si surface. The N-plasma was interrupted when the substrate temperature stabilized at the growth temperature of 230°C. After the N-plasma treatment the substrate surface showed a RHEED pattern with bulk 1x1 streaks and a blurred 7x7 reconstruction, as observed in Fig. 1(b). We observed that the mere exposure of the Si(111) surface to a flux of N_2 had no appreciable effects on the surface reconstruction. Thus the changes in the RHEED pattern observed in Fig. 1(b) should be caused by the reaction of the active nitrogen plasma with the Si surface.

4. Results and discussion

Fig. 1(c) shows the RHEED pattern obtained after 8 ML of ZnSe grown by conventional MBE directly on Si(111) without the N-plasma treatment. The intense bulk-spots and the diffuse background are indicative of a three-dimensional growth mode. With further growth, crystal defects became evident by the appearance of extra-spots indicating the formation of twinned regions, as observed in the RHEED pattern of Fig. 1(d) that corresponds to the growth of 30 ML of ZnSe. Fig. 2(a) shows the behavior of the RHEED specular spot intensity during the initial stages of ZnSe MBE growth on Si without the N-plasma surface treatment. The difficulty in obtaining a smooth ZnSe growth by this technique is illustrated by the strong decrease in intensity observed in this figure. The three-

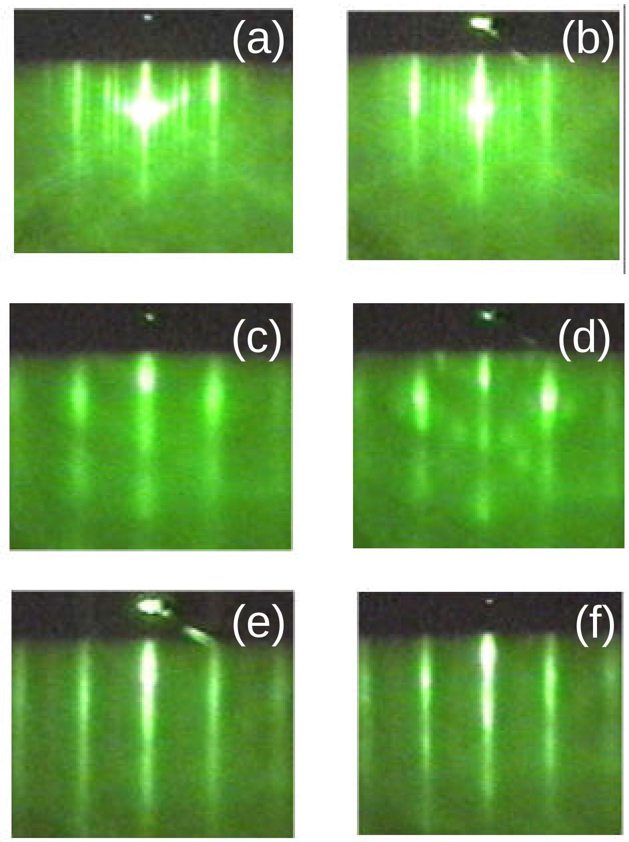

Fig. 1 RHEED patterns of: (a) clean Si(111) surface, (b) N-plasma treated Si(111) substrate, (c) 8 ML and (d) 30 ML of ZnSe grown by conventional MBE directly on an untreated Si(111) substrate, (e) 8 ML and (f) 30 ML of ZnSe grown by pulsed MBE on an N-plasma treated Si(111).

dimensional islands resulting from the direct MBE growth on untreated Si substrates are shown in Fig. 3(a).

Next we will show the great improvement in the epitaxy obtained when growing on a Si surface treated with N-plasma. Fig. 1(e) shows the RHEED pattern obtained after 8 ML of ZnSe grown by pulsed MBE on an N-plasma treated substrate. The RHEED pattern looks very streaky, and moreover a 2-fold reconstruction can be observed suggesting a two-dimensional growth mode and an atomically ordered surface. For thicker layers the streaky patterns were conserved as observed in Fig. 1(f), which corresponds to 30 ML of ZnSe. The improved epitaxy is evident when comparing these RHEED patterns with the corresponding patterns obtained by direct MBE on untreated substrates (Figs. 1(c) and (d)). The RHEED patterns in Figs. 1(e) and (f) have a low background and are much streakier, indicating a flat surface. The definitive prove of the two-dimensional nucleation obtained by this

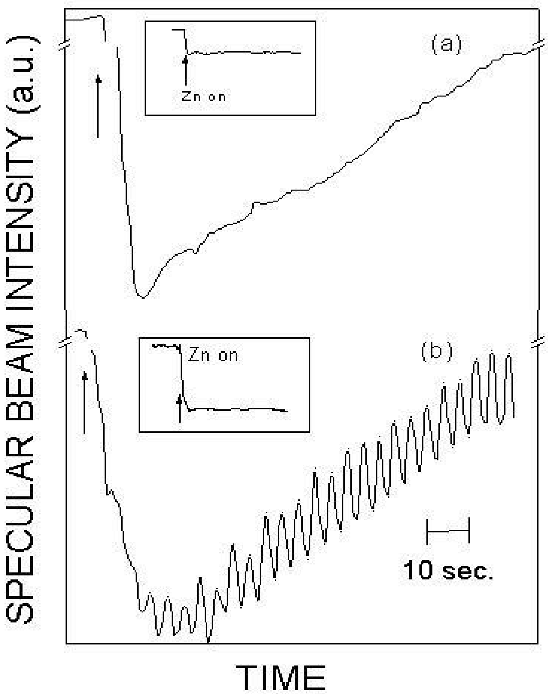

Fig. 2 Behavior of the RHEED specular spot intensity during the ZnSe growth on Si(111). (a) MBE growth on an untreated Si substrate, (b) pulsed MBE growth on an N-plasma treated Si substrate. The arrows indicate the start of the growth. The insets show the changes in the RHEED specular spot intensity when the (a) untreated- and (b) N-plasma treated substrate surface was exposed to the Zn flux.

technique was the clear presence of large amplitude RHEED oscillations as shown in the Fig. 2(b). Moreover, Auger measurements revealed a better ZnSe-coverage for the N-plasma treated Si surface, supporting the idea of a layer by layer growth promotion by this technique. The AFM image in Fig. 3(b) confirmed the flatter ZnSe surface obtained on the N-plasma treated Si surface.

On the other hand, we observed that the lattice mismatch relaxation process was also affected by the different ZnSe growth mode on the N-plasma treated- and untreated Si substrates. From the spacing of the diffraction lines in the RHEED patterns, we estimated the changes in the lattice constant as a function of ZnSe thickness. For both types of substrates the lattice relaxation starts at the beginning of growth, as shown in Fig. 4. The lattice constant of ZnSe grown on N-plasma treated substrates reaches its relaxed value at about 3 ML of growth. However, the lattice relaxation process for layers grown on untreated substrates seems to be slower. This could be explained by the three-dimensional growth obtained on this type of substrates. It is known that part of the lattice misfit strain can be relaxed at the boundaries of three dimensional islands, thus thicker layers are required to complete the lattice relaxation process[14].

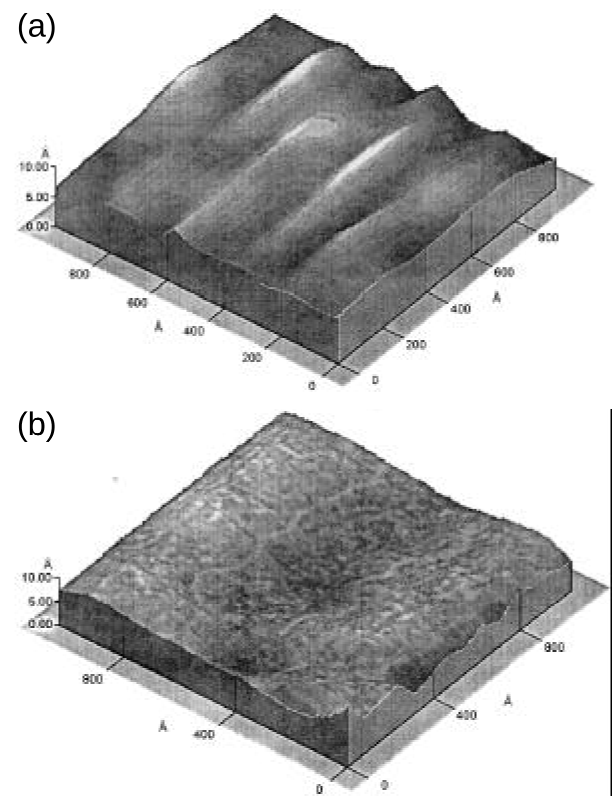

Fig. 3 Atomic force microscopy images of (a) 30 ML of ZnSe grown by conventional MBE directly on an untreated Si substrate, (b) 30 ML of ZnSe grown by pulsed MBE on an N-plasma treated Si substrate.

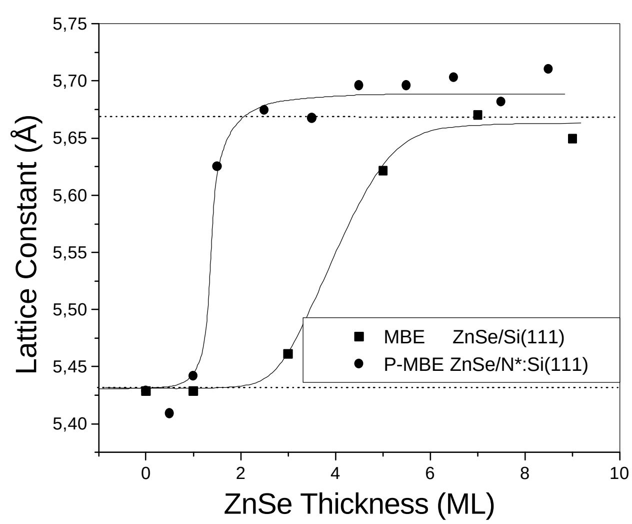

Fig. 4 Lattice relaxation of ZnSe layers on ( ) untreated- and (●) N-plasma treated Si(111) substrates.

Here it is worth to comment that we observed an improvement on the ZnSe epitaxy by using the pulsed MBE growth mode on Si substrates without the N-plasma treatment, but it was not as important as that obtained on the N-plasma treated Si substrates. We observed only slight traces of reconstruction on a spotty RHEED pattern, and very small damped oscillations of the specular RHEED spot intensity. These results show that the N-plasma treatment and not the growth technique, is playing the most important role in the promotion to a 2D growth of ZnSe on Si. A change in the bonding conditions at the interface is indicated by the behavior of the RHEED specular spot intensity when the untreated Si(111), and the N-plasma treated Si(111) surfaces were exposed to Zn. A small change in the RHEED specular spot intensity was observed when the Si surface was exposed to the Zn flux (see the inset of Fig. 2(a)), which could be due to the very small sticking coefficient of Zn on the bare Si surface[4]. In contrast, the inset in Fig 2(b) shows the larger decrease in the RHEED specular spot intensity when the N-plasma treated Si substrate was exposed to Zn. This result suggests an increase in the Zn sticking coefficient on the N-plasma treated Si surface.

The two dimensional growth could be induced by the formation of a nitrogen interlayer that avoid the formation of the $SiSe_x$ compound, and could balance the electric charge at the ZnSe/Si interface (problems mentioned in the section 1), thus allowing the growth of a smooth ZnSe epilayer. Note that the presence of an arsenic monolayer at the ZnSe/Si(100) interface has been reported to yield a better film quality[10,15]. It was suggested that this As monolayer makes that all interface bonds have two electrons, thus keeping charge balance at the interface[8]. Nitrogen atoms have the same number of valence electrons as As atoms have, thus a similar effect could be expected for a Si(100):N interface. For the (100) interface a complete nitrogen monolayer at the interface is required[8], however for the (111) interface a sub-monolayer amount of nitrogen is enough. For example, charge balance occurs when the nitrogen atoms displaces Si atoms and take the place of 50% of the surface sites, so the N atoms share three bonds to the substrate, as shown in Fig. 5(a). This geometry is suggested by bonding experiments on other column V elements (like As) on Si(111) surfaces[16]. In this way the growth could smoothly continue with a complete monolayer of Zn atoms bonded to a surface formed by Si and N, as illustrated in Fig. 5(b). A different sub-monolayer amount of N could be possible depending on the particular atomic geometry at the Si surface. The partial coverage of the Si(111) surface with nitrogen could be reflected by the blurred 7x7 reconstruction after the N-plasma treatment, as shown in Fig. 1(b). Further experiments to investigate the chemical bonding at the interface are underway.

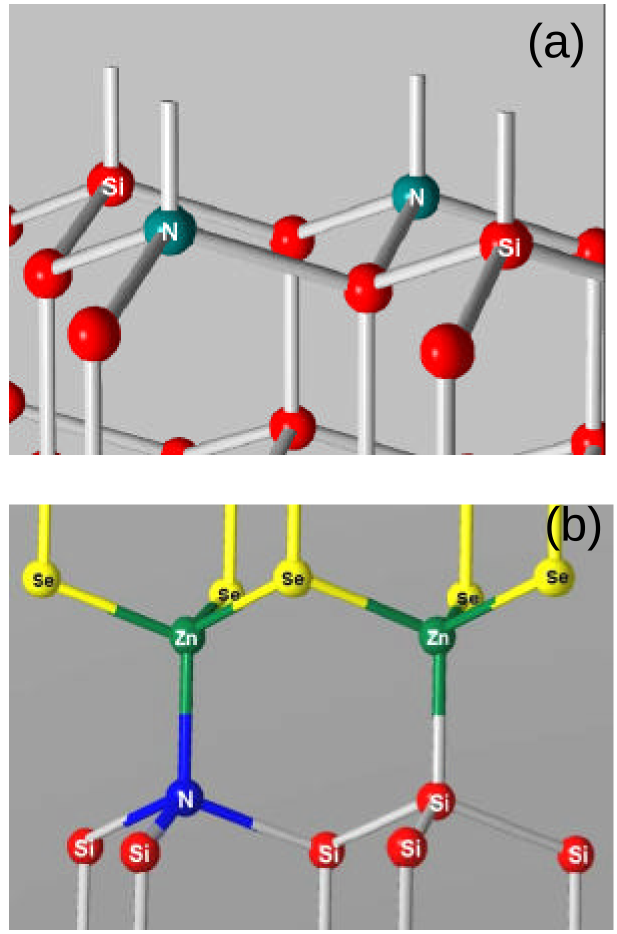

Fig. 5 Schematic picture of a possible atomic arrangement (a) of the Si surface after the N-plasma treatment and (b) in the early stages of the ZnSe growth.

5. Conclusions

We investigated the effects of substrate surface irradiation with an N-plasma on the initial stages of the growth of ZnSe on Si(111). The use of the N-plasma surface treatment allowed us to obtain a two dimensional growth in this heteroepitaxial system. This improvement could be caused by nitrogen passivation of the Si surface, reducing its strong reactivity to Se. The formation of an interlayer that could balance the electric charge at the ZnSe/Si interface is also possible.

Acknowledgments

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