JOURNAL OF MATERIALS SCIENCE **36** (2001) 3801–3803

The study of highly crystalline ZnSe growth on porous silicon

C. C. CHANG, C. H. LEE
Department of Electrical Engineering, National Taiwan Ocean University, Keelung, Taiwan
E-mail: ccchang@mail.ntou.edu.tw

The objective of this study relates to producing a ZnSe epilayer on porous silicon. In the subsequent process, ZnSe having a direct energy gap of 2.68 eV at room temperature was grown on porous silicon under differing anodization conditions utilizing chemical vapor deposition techniques, resulting in the successful growth of a single crystal ZnSe epilayer on the porous silicon substrate. The characteristics of the epilayer were then analyzed by X-ray diffraction and photoluminescence. The photoluminescence spectrum of the single ZnSe epilayer exhibited good emission properties at 444 nm (2.792 eV), 457 nm (2.718 eV), 478 nm (2.594 eV), and 574 nm (2.16 eV). © *2001 Kluwer Academic Publishers*

1. Introduction

Uhlir [1] and Turner [2] found that bulk silicon can be transformed into a material consisting of a network of pores by utilizing an anode in hydrofluoric acid. A major application of porous silicon is in silicon-on-insulator (SOI) technology [3–5], wherein active devices are dielectrically isolated utilizing the oxidation of the underlying porous silicon. In addition, this material has drawn significant attention after Canhan reported recently that porous silicon emits visible light at room temperature [6] in that the discovery demonstrated the suitability of the substance for Si-based optoelectronic devices [7].

Wide band-gap II-VI compounds were previously more important in research on blue-green optoelectronic devices [8, 9]. However, since the band-gap of ZnSe is 2.68 eV at room temperature [10] and is within the blue region of the optical spectrum, there is renewed interest in ZnSe. This study is an attempt to grow a heteroepilayer of ZnSe on porous silicon substrates utilizing chemical vapor deposition (CVD) techniques, with the assumption that the process will be useful in the development of low-cost, short wavelength optoelectronic integrated circuit (OEIC) devices.

2. Experimental procedure

A p-type (111) ($\rho = 3\ \Omega$cm) silicon substrate was utilized for epitaxial purposes. Substrates were placed in a Teflon container which was then filled with an electrolyte having one of a varying of HF:C_2H_5OH ratios [11, 12]. Each substrate was connected to a power source via a bottom electrode and a Pt electrode. A constant current was then passed through the substrate to form a thin porous layer on the surface of silicon substrate. Following this anodization process, the porous silicon substrate was placed in a vessel which was positioned in a chemical vapor deposition (CVD) system. Pure H_2 was injected into the CVD system after the system was evacuated down to 25 mtorr. When the CVD system pressure reached one atmosphere, the substrate temperature was increased to 450°C in a 350 sccm hydrogen flux, at which point the ZeSe buffer layer deposition was initiated. After the ZnSe buffer layer was deposited on the porous silicon layer, the substrate temperature was increased to 650°C for epilayer growth, with the growth period for the ZnSe epilayer set at 45 minutes. Following the growth of the epilayer on the substrate, the characteristics of ZnSe thin films were analyzed utilizing X-ray diffraction (XRD) and photoluminescence (PL).

3. Results and discussion

In the analysis of the ZnSe deposition layer, the following equation for intensity, I, was utilized for the evaluation of the degree of preferred (111) orientation:

$$I = \frac{\frac{\alpha}{100}}{\frac{\alpha}{100} + \frac{\beta}{70} + \frac{\gamma}{44}}$$

Where α is the (111) peak count, β is the (200) peak count, and γ is the (311) peak count.

The values of 100, 70 and 44 are the standard intensities as defined by the Joint Committee on Powder Diffraction Standards. Thus, if I equals one, the epilayer is a (111) single crystalline structure. In this experiment, the parameters that influence the epilayer characteristics included the porous layer and buffer layer conditions. With the buffer layer deposition period fixed at 15 minutes, porous layer conditions were varied to change the quality of the epilayer. The parameters that determined porous layer characteristics included anodization time, HF : C_2H_5OH ratio, and current density. These experiments demonstrated that a

ZnSe epilayer of a near single crystalline structure could be produced by varying the HF : C_2H_5OH ratio and current density alone. Fig. 1 illustrates the relationship between I and the p-substrate current density with a HF : C_2H_5OH ratio of 1 : 1 and an anodization time of 30 seconds. As shown in the figure, a current density of 30 mA/cm^2 yielded a more optimal epilayer quality. Depicting the relationship between I and the p-substrate HF : C_2H_5OH ratio, Fig. 2 illustrates that with a current density of 30 mA/cm ^{2} and HF : $C_2H_5OH = 3 : 2$ a near single crystalline ZnSe epilayer can be produced. Fig. 3 is the XRD pattern of the single crystalline ZnSe epilayer on porous silicon. The crystallinity of the ZnSe epilayer is very good as evidenced by the sharp peaks for which full width at half minimum (FWHM) is 0.2°. In addition, the silicon (111) peak also appears in the XRD pattern and is attributed to the extremely thin ZnSe buffer layer and epilayer (~0.2 μm). From above, it is demonstrated that a ZnSe epilayer of near single crystalline structure could be produced by varying the HF : C_2H_5OH ratio and current density. In addition, Fig. 4 is the relationship between I and anodization time. It shows that varying the annodization time changes the epilayer quality also. Finally, the relationship between I and buffer layer deposition time is indicated in Fig. 5, where different buffer layer thicknesses determine the crystalline structure. Figs 4 and 5 illustrate that anodization time and buffer layer thickness parameters also determine epilayer quality, and that near single crystalline epilayers are possible by varying a greater range of different parameters; further experimentation concerning this aspect is ongoing. In addition, the PL experiments were conducted with an argon laser (365 nm wavelength) and a grating monochromator. The measurement temperature of samples was set at 10 K. Fig. 6 is the measuring results that the PL

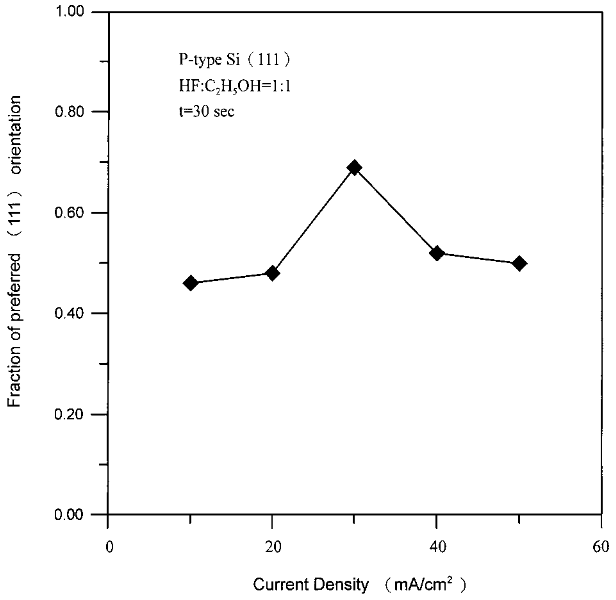

Figure 1 The relationship between the preferred (111) orientation and current density for p-substrate.

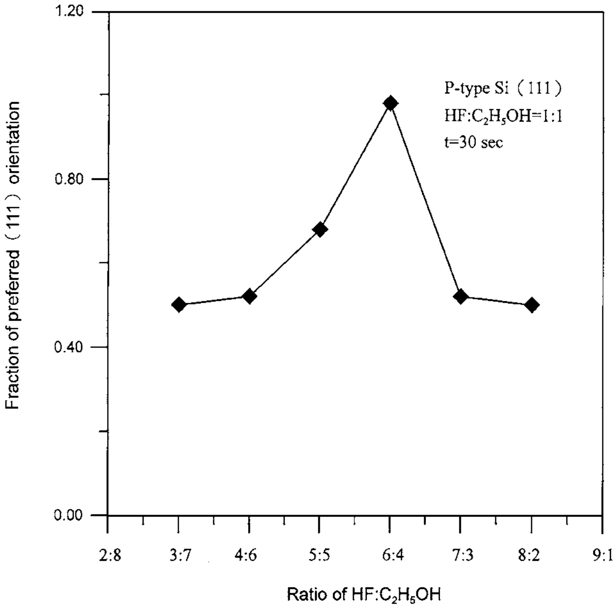

Figure 2 The relationship between the preferred (111) orientation and the ratio of HF : C_2H_5OH for p-substrate.

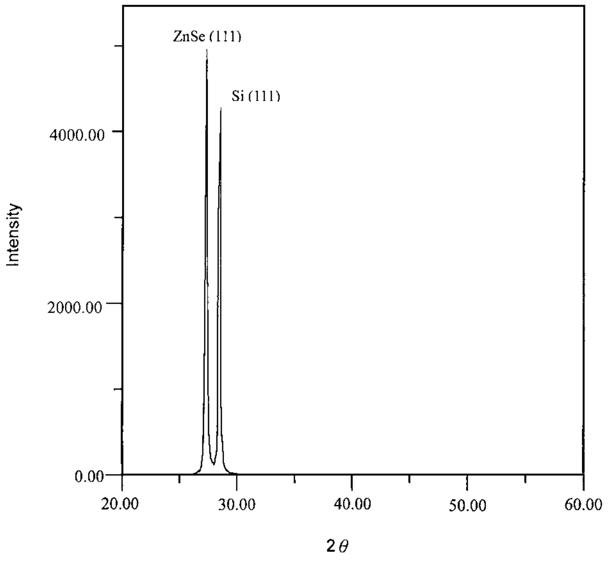

Figure 3 The XRD pattern of ZnSe single crystal thin film.

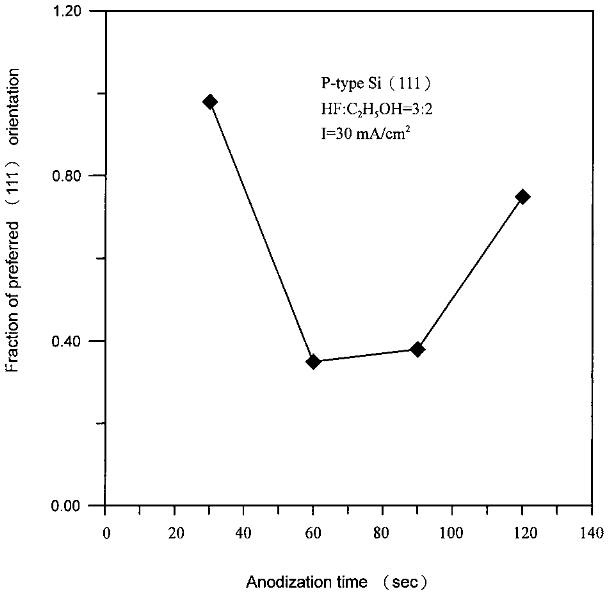

Figure 4 The relationship between the preferred (111) orientation and anodization time for p-substrate.

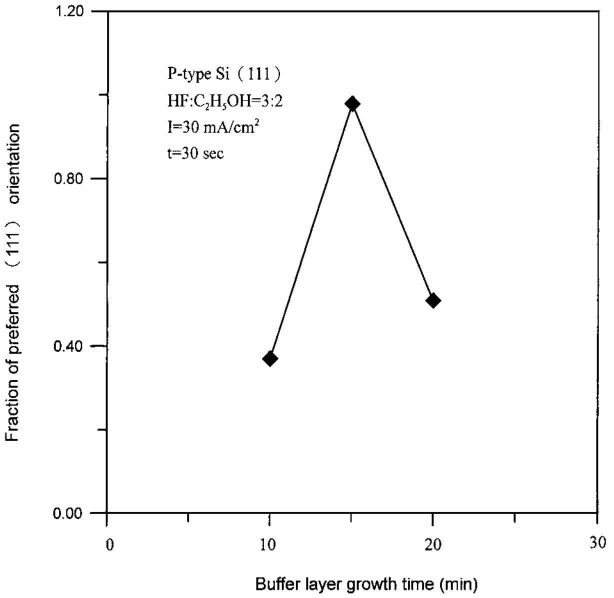

Figure 5 The relationship between the preferred (111) orientation and buffer layer grown time.

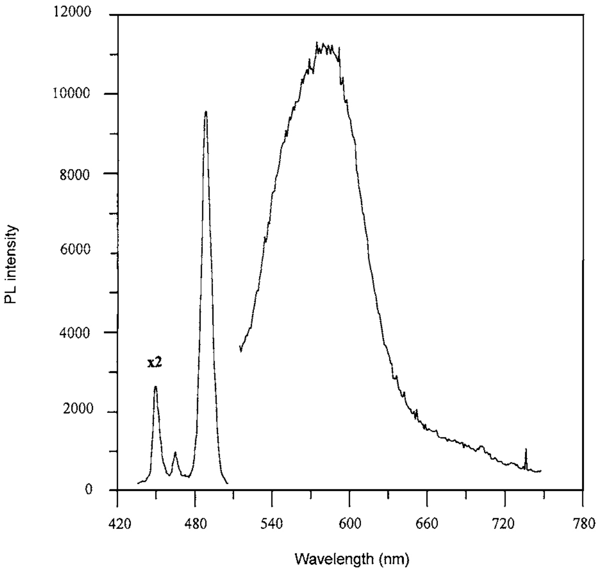

Figure 6 The PL spectrum of ZnSe single crystal thin film at 10 K.

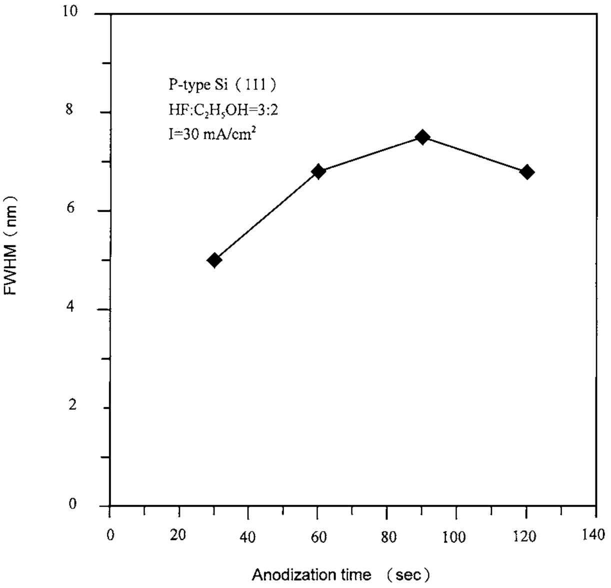

Figure 7 The relationship between FWHM and anodization time for p-substrate.

spectrum of the single crystalline ZnSe thin film on porous silicon with the ZnSe epilayer grown on p-type (111) Si substrate at current density 30 mA/cm^2, anodization time 30 seconds, and HF : C_2H_5OH ratio of 3 : 2. The PL spectrum shows four peaks at 444 nm, 457 nm, 478 nm, and 574 nm. The 457 nm peak is attributed to the radiative recombination of an electron and a hole bound to a donor-acceptor pair (D-A pair), while the 444 nm peak is the result of excitonic recombination [8]. The 478 nm peak is probably due to silicon impurities diffused into the ZnSe epilayer. The peak of broad-band emission, the 574 nm (2.16 eV) reading is the deep-level emission [13]. Fig. 6 indicates that the ZnSe epilayer has blue emission characteristics, though the broad-band emission must still be suppressed. Fig. 7 is the relationship between the 457 mm peak FWHMs and the HF : C_2H_5OH ratio, where optimal quality was obtained at an HF : C_2H_5OH ratio of 3 : 2, a current density of 30 mA/cm^2, and an anodization time of 30 seconds, with the resulting characteristics resembling the other crystalline structures analyzed by XRD.

4. Conclusion

A single crystalline ZnSe epilayer was successfully grown on a porous silicon substrate utilizing a CVD system. The optimal anodization conditions for the p-substrate during the growing of the ZnSe epilayer on the silicon substrate were an HF : C_2H_5OH ratio of 3 : 2 and a current density of 30 mA/cm^2. Indicative of good emission properties, four peaks at 444 nm, 457 nm, 478 nm, and 574 nm were observed in the PL spectrum of the resulting single crystalline ZnSe epilayer.

References

1. A. UHLIR, *Bell Syst. Tech. J.* **35** (1956) 333.
2. D. R. TURNER, *J. Electrochem. Soc.* **105** (1958) 402.
3. G. BOMCHIL, A. HALLIMAOUI and R. HERINO, *Microelectron. Eng.* **8** (1988) 293.
4. K. IMAI and H. UNNO, *IEEE Trans. Electron Devices ED-31* (1984) 291.
5. R. L. MEEK, *J. Mater. Sci.* **118** (1971) 437.
6. L. T. CANHAM, *Appl. Phys. Lett.* **57** (1990) 1046.
7. P. STEINER, F. KOZLOWSKI and W. LANG, *IEEE Electron Devices Letters* **14** (1993) 317.
8. M. YAMAGUCHI, A. YAMAMOTO and M. KONDO, *J. Appl. Phys.* **48** (1977) 5237.
9. J. C. BOULEY, P. BLANCONNIER, A. HERMAN, P. HENOC and J. P. NOBLANC, *ibid.* **46** (1976) 3549.
10. M. CARDONA, *ibid.* **132** (1961) 2151.
11. M. I. J. BEALE, N. G. CHEW, M. J. UREN, A. G. CULLIS and J. D. BENJAMIN, *Appl. Phys. Lett.* **46** (1985) 86.
12. Y. KANG and J. JORNE, *ibid.* **62** (1993) 2224.
13. H. G. GRIMMEISS and C. OVREN, *J. Appl. Phys.* **48** (1977) 5122.

Received 1 September 1999
and accepted 22 January 2001