Band-edge photoluminescence from pseudomorphic $Si_{0.96}Sn_{0.04}$ alloy

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Band-edge related photoluminescence from a strained $Si_{0.96}Sn_{0.04}$ alloy grown by molecular beam epitaxy on Si(100) substrate has been seen for the first time. We report band-edge related photoluminescence from a compressively strained pseudomorphic $Si_{0.96}Sn_{0.04}$ alloy. The luminescence observed consisted of two dominant features, a well-resolved band-edge luminescence consisting of a no-phonon and a transverse optical phonon replica, and a deep-level broad luminescence peak around 770 meV. The band-edge feature is attributed to a no-phonon free excitonic recombination in the binary alloy and exhibits a near linear power dependence. We also observe a red shift of the energy gap of $Si_{0.96}Sn_{0.04}$ alloy with respect to Si, which corresponds to the bulk alloy effect. © *1996 American Institute of Physics.* [S0003-6951(96)01422-2]

Recently, there has been a lot of attention focused on the optical and electronic properties of group IV alloys grown on silicon.[1] The most studied system is the $Si_{1-x}Ge_x$ binary alloy[2–4] but recently the binary $Si_{1-x}C_x$,[5,6] $Ge_{1-x}C_x$,[7,8] the ternary $Si_{1-x-y}Ge_xC_y$ (Ref. 9) alloys, and quaternary alloys of $Si_{1-x-y-z}Ge_xC_ySn_z$ (Ref. 10) have received some attention as well. The binary IV–IV alloy $Si_{1-x}Sn_x$ has also been studied.[10,11] The majority of the previous investigations was concerned with the preparation and characterization of amorphous films, but recently there have been a few studies in the growth of crystalline thin films of $Si_{1-x}Sn_x$ and $Si_{1-x-y}Sn_xC_y$ alloys.[10,11] The amorphous films were prepared by magnetron sputtering,[12] rf sputtering,[13–15] chemical vapor deposition,[16] dc triode sputtering,[17] e-beam Knudsen cell evaporation,[18] and recently pulsed laser deposition,[19] with various degrees of success. The crystalline thin films have been prepared previously by a combination of ion implantation and solid-phase epitaxy (SPE).[20,21] This method of synthesis, however, was plagued with residual ion damage and the inability to produce sharp interfaces. Recently, high-quality pseudomorphic crystalline thin films of $Si_{1-x}Sn_x$ alloys have been prepared by molecular beam epitaxy (MBE).[10,11] These previous studies have all indicated that it is very difficult to stabilize Sn in the Si alloy lattice. This is mainly due to the following reasons. There is a large difference in the Si and Sn lattice parameters. Grey tin has a lattice parameter of 6.489 Å and Si a value of 5.431 Å, resulting in a 19.48% lattice mismatch. Grey tin (α-Sn) crystallizes in the diamond structure and at 13.2 °C it transforms into the tetragonal structure of metallic white tin (β-Sn). It is possible to incorporate a large concentration of Sn in a disordered Si:H matrix,[12,16] but Sn has a very low solid solubility in crystalline silicon[22] ($\sim 5\times 10^{19}$ cm^{-3}). The incorporation of isoelectronic Sn into silicon would result in the ability to engineer the band gap, which would lead to changes in the optical and electrical properties of the material. According to recent theoretical calculations,[23] $Si_{1-x}Sn_x$ alloy would ideally have a band gap between that of silicon and tin, 0.08 and 1.153 eV, which is very important for IR detector applications. Also, the band gap was predicted[23] to be direct for the compositional range of $0.9<x<1$ and indirect for all others. Strained layers of $Si_{1-x}Sn_x$ alloy semiconductors would find numerous applications in electronic and optoelectronic heterostructures. To our knowledge, the optical luminescence properties of pseudomorphic $Si_{1-x}Sn_x$ alloys grown on Si substrates have not been reported in any previous studies.

For the first time, we report in this letter the band-edge photoluminescence of compressively strained $Si_{1-x}Sn_x$ alloy grown by molecular beam epitaxy (MBE) on Si(100) substrate. The luminescence at 6 K consisted of a no-phonon (NP), a transverse optic (TO) phonon, and a deep-level broad luminescence peak. The band-edge feature is attributed to a no-phonon free excitonic recombination in the binary alloy and is found to exhibit a near linear power dependence. The band-gap energy variation of the alloy is determined from the position of the NP line. This is found to be in good agreement with the effect of Sn in the bulk band gap but appears to be redshifted due to residual strain.

The details of the solid source MBE growth of the $Si_{1-x}Sn_x$ layer are described elsewhere.[10] After an RCA type clean, the (100) silicon wafers were cleaned *in situ* at over 950 °C to desorb the chemical oxide. A thin 20 nm Si buffer layer was grown initially followed by the growth of the $Si_{1-x}Sn_x$ layer. The Si flux was feedback controlled and the Sn flux was controlled through the temperature control of the Knudsen cell. The $Si_{1-x}Sn_x$ layer growth temperature was 500 °C and the layer thickness was 150 nm. The growth conditions were optimized to maximize the incorporation of Sn on Si lattice sites. The layer composition were measured by Rutherford backscattering spectrometry (RBS) and con-

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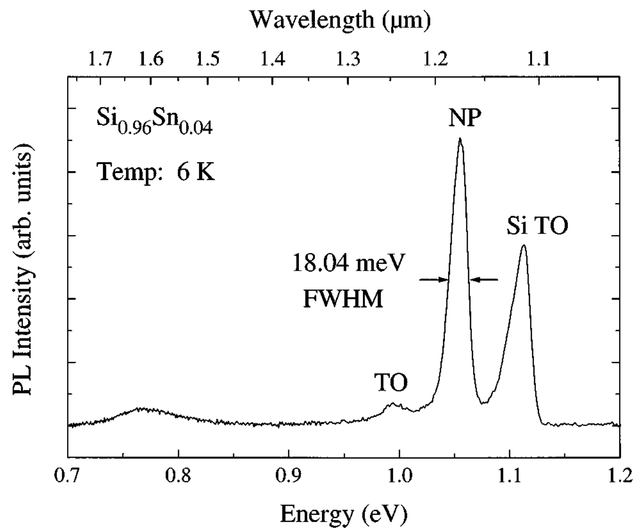

FIG. 1. PL spectra at 6 K of a $Si_{0.96}Sn_{0.04}$ alloy grown by MBE showing band-edge (NP) and deep-level luminescence. Laser excitation consisted of Ar^+ ion laser with a laser spot size of 0.68 mm diameter.

firmed by x-ray diffraction analysis (XRD). X-ray diffraction measurements of the layer confirmed the substitutional incorporation of Sn and that the layer was pseudomorphic and compressively strained.[10] Alloy decomposition through precipitation of tin atoms into metallic β-Sn was not observed at a growth temperature of 500 °C, unlike that observed by Shiryaev *et al.*[11] after high-temperature (1000 °C) annealing.

Photoluminescence (PL) spectra were recorded in standard lock-in configuration, using a dispersive 1 m high-resolution Jarell–Ash (Czerny–Turner) monochromator and detected by a liquid-nitrogen-cooled Ge *p-i-n* photodetector (North Coast EO-817L). The samples were mounted on a cold finger in a temperature variable helium-flow cryostat. The excitation was provided by a multi-line cw Argon ion laser (488–514 nm) with pump intensities between 0.3 and 5 W/cm^2. Data collection and lock-in amplification were controlled by a desktop computer.

PL spectra for the $Si_{0.96}Sn_{0.04}$ sample is presented in Fig. 1. The luminescence consists of a low intensity deep-level luminescence and two band-edge peaks. The most intense peak at 1.055 eV is ascribed to a NP transition, whereas the second peak at 0.9938 eV is redshifted by 61 meV and corresponds to its transverse-optic (TO) Si–Si phonon replica. This NP transition is shifted 98 meV below that observed in pure Si.[24] We attribute this redshift to the reduction in band gap of the binary SiSn alloy. However, the observed NP transition is also shifted 54.8 meV below an expected 1.1106 eV luminescence position using Vegard's Law for a SiSn alloy composition with 4% Sn. This additional redshift we attribute to the reduction in the band gap caused by residual strain in the pseudomorphic layer. The observed luminescence peak at 1.114 eV is attributed to a Si transverse-optical (TO) phonon transition within the Si substrate. Also, a deep-level broadband luminescence is observed around 770 meV. Similar deep-level broadband luminescence has been observed in SiGe, SiC, and SiGeC layers grown by MBE and has been attributed to localized excitons in a strain field created by Ge platelets,[25] the emission of deep pseudoacceptors,[26] or to carbon-oxygen complexes,[5] respectively. It should also be noted that the samples were measured at various times over an eight-month period, and the luminescence spectra was very consistent.

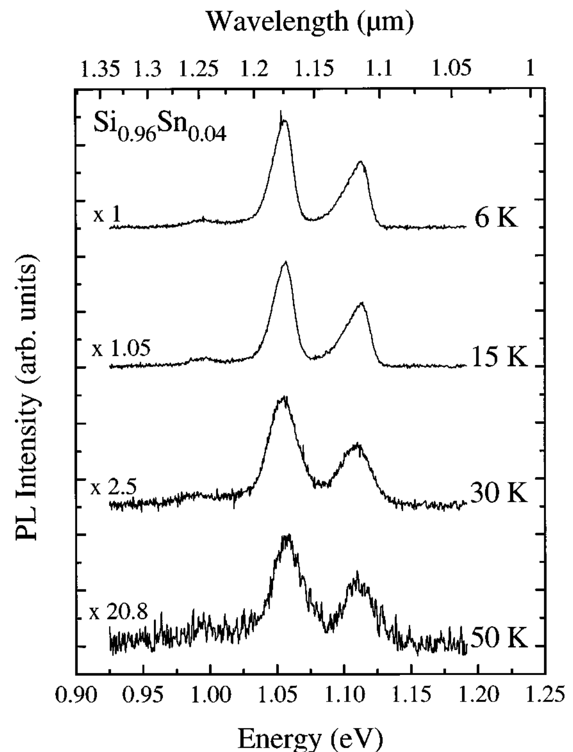

FIG. 2. PL spectra of $Si_{0.96}Sn_{0.04}$ alloy at 6, 15, 30, and 50 K.

The temperature dependence of the PL spectra was also measured. Temperature dependence of the PL spectra is shown in Fig. 2 by plotting the luminescence at 6, 15, 30, and 50 K. It was observed that the luminescence persisted past 50 K, but was degraded in intensity. As the temperature was increased the PL intensity decreased and the linewidth broadened in the direction of higher energy. This type of linewidth behavior is the characteristic of Maxwell–Boltzman distribution. The energy position of the NP peak remained constant as the temperature was increased. PL temperature dependence of this nature is the characteristic of free-exciton (FE) recombination. Therefore, we attribute the line labeled NP at 1.055 eV as due to a no-phonon free-exciton recombination. The full width at half maximum of the NP line is 18.04 meV at 6 K, which is rather broad compared to the intrinsic FE thermal linewidth, but this could be attributed to statistical fluctuations in the atomic distributions of the alloy as discussed by Robbins *et al.*[27]

The laser power dependence of the band-edge luminescence and the deep-level peaks are shown in Fig. 3. The peak labeled NP shows an almost linear increase in intensity with increasing laser power, while the deep-level broadband shows a sublinear dependence. Linear power dependence is a characteristic of a no-phonon free-exciton recombination. The square-root dependence of the deep-level band indicates that a recombination center is involved in the recombination process. This behavior is a characteristic of localized excitons bound to an isoelectronic trap in Si.[28]

In conclusion, we have reported band-edge related pho-

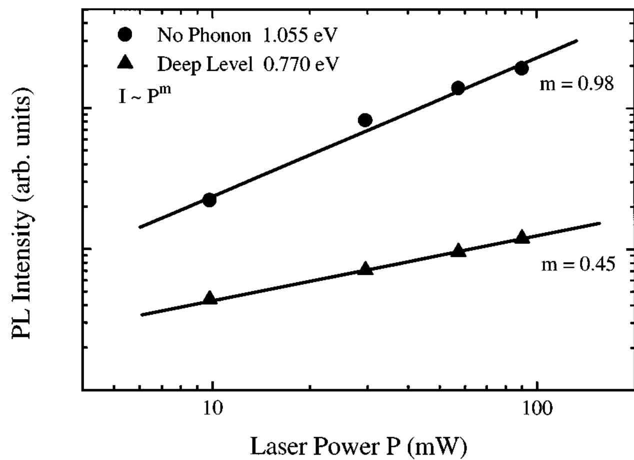

FIG. 3. Intensity if the NP transition and the deep-level transition for a $Si_{0.96}Sn_{0.04}$ alloy grown by MBE as a function of laser power.

toluminescence from a pseudomorphic $Si_{0.96}Sn_{0.04}$ alloy grown by MBE. Two general features have been observed for the first time, a deep-level broadband luminescence and a band-edge luminescence consisting of a NP and TO replica. The band-edge feature increases almost linearly with increasing laser power while the deep-level broadband showed a square-root dependence. The redshift of the energy gap was attributed to the bulk alloy effect and to residual strain.

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