Observation of anomalously polarized photoluminescence in alternating nanocrystalline Si-amorphous Si multilayers

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Polarization properties of visible photoluminescence (PL) from alternating hydrogenated nanocrystalline silicon-amorphous silicon multilayers excited with linearly polarized light are examined. The PL is almost linearly polarized in the direction perpendicular to the polarization of excitation light, independent of the sample orientation. The degree of linear polarization $\delta$ negatively increases with decreasing emission energy, reaching a maximum of $\sim 90\%$ on the low-energy side, and a different temperature dependence is observed. In addition, it was found that the sample with large structural inhomogeneity displays low PL efficiency and large $\delta$. Since the obtained PL spectra show no crystallite size dependence of the peak energy and fine structures, we attribute these anomalous polarization properties to the radiative recombination of carriers confined in the interfacial region of optically anisotropic and randomly distributed Si:H nanocrystals.

Since the discovery of its visible room-temperature photoluminescence (PL), porous Si (PS) has been widely investigated experimentally and theoretically due to its large applications potential in optoelectronics.\(^1,2\) The quantum-confinement effect of photoexcited carriers within nanocrystallites was mainly proposed to be responsible for the visible PL. However, the microscopic details are complicated and have not yet been completely understood. Recently, much attention has been paid to polarization properties of the PL, because a study on this phenomenon can provide an important insight into the PL origin from microstructural viewpoint. Starukhin et al.\(^3\) and Andrianov et al.\(^4\) reported that the visible PL of PS has a property to retain the linear polarization of excitation light. The degree of linear polarization can reach $\sim 30\%$ under excitation of a linearly polarized light. They attributed this result to the microstructural anisotropy in PS. Koyama and Koshida\(^5\) further presented some characteristic phenomena of the dependence of the polarization retention degree on both excitation wavelength and temperature by examining the polarization property of the PL. These results are attributed to the radiative recombination of excitons localized within optically anisotropic and randomly distributed Si nanocrystallites. Similar to open semiconductor quantum well wires, Kovalev et al.\(^6\) reported that unusual behavior of the PS polarization can be related to the nonsphericity of the Si nanocrystals and arises from the large difference between the dielectric constants of the anisotropic semiconductor nanocrystals and the surrounding medium. So far, although many models have been presented to describe the polarization mechanism of the PL, the existing data and interpretations are still controversial. Further work is needed to clarify this issue.

In previous literature,\(^7\) we reported the observation of stable PL in layer-by-layer deposited hydrogenated nanocrystalline Si-amorphous Si (nc-Si:H/a-Si:H) multilayers (ML’s) without any postprocessing. According to the Raman scattering results,\(^8\) we attributed the PL to the quantum confinement of nc-Si:H nanocrystallites in the nanocrystalline sublayers. However, the essential origin of the PL is still unclear and much work is needed to address this question. In this paper, we report the polarization property of the PL from this kind of ML. Some significant results, which are different from those reported from earlier authors, were obtained. We will discuss all the results.

Polished crystal Si wafers with (100) orientation, $p$ type and 1–3 $\Omega$ cm resistivity were used as sample substrates. ML’s were deposited with a conventional diode glow discharge system with capacitance electrodes. During sample deposition, the substrate temperature was controlled at 300 °C, and the rf power density of glow discharge at 0.44 W/cm$^2$, but it was interrupted at each step of individual layer deposition to keep the interfaces abrupt. Two typical ML’s (A and B) were prepared with 50 periods. The thickness of single nc-Si:H and a-Si:H sublayers in sample A were 3 and 8 nm and those in sample B were 2.2 and 8 nm, respectively. According to the Raman scattering results,\(^8\) the corresponding mean crystallite sizes in samples A and B were 3.5 and 2.2 nm. Nanocrystallites in sample A have more complicated shapes and boundaries than those in sample B.\(^9\) From the x-ray diffraction results,\(^10\) we found...
that sample A has a larger fluctuation in the thickness of the individual periods and more voids or holes than sample B. These features indicate that sample A has a more inhomogeneous structure than sample B. Details of sample preparation have been described previously. \(^7,11\)

A schematic drawing of the experimental arrangement for the PL measurements used in this work has been described previously. \(^12\) A linearly polarized 514.5-nm line of an Ar laser was introduced normally to the sample surface. Its polarization direction can be changed by rotating a half-wavelength plate and is always parallel to the sample surface. The emission was collected through a focusing lens on a SPEX 1403 monochromater and its polarization direction was examined by an analyzer. The sample and analyzer can only be rotated in the plane perpendicular to optical axis of the measurement system. A cooled RCA 3103 photomultiplier tube and photon counting electronics interfaced to a microcomputer were used to analyze the data. Under our experimental conditions, all the measured PL spectra were corrected for the polarization-dependent response of the measurement system. \(^13\) During PL measurements, ML’s were kept in a vacuum to avoid significant sample degradation due to laser irradiation.

Figure 1 shows the room-temperature PL spectra of samples A and B, measured under the condition of no analyzer. The two spectra are very broad (\(\sim 0.4\) eV at full width at half maximum) and clearly show two PL peaks around \(\sim 1.7\) and 1.54 eV with intensities about 2 orders of magnitude lower than that of ordinary porous Si. The PL intensity is higher in sample B than in sample A, indicating that the PL intensity depends on the sample homogeneity. \(^10\) the crystallite sizes, and volume fraction of the crystalline. \(^8\) Since the quantum size effect suggests that the smaller the crystallite size, the higher the energy of the PL peak, the fact that the energy (1.68 eV) of the PL peak in sample B with a small crystallite size is lower than that (1.72 eV) in sample A with a large size is indicative of no crystallite size dependence of the peak energy. This result means that the PL process in our samples has an origin other than the quantum confinements on the c-Si cores. The energy of the 1.54-eV peak hardly changes in the two samples. It may come from the growth interruption during sample deposition \(^14\) and thus is closely related to the structure of the interface between nc-Si:H and a-Si:H sublayers. According to the calculation by Ren and Dow, \(^15\) the band gap of crystallites of 3-nm diameter with hydrogenated surfaces is 1.5 eV. The obtained PL peak energies are larger than the theoretical band gap. This indicates that a region containing a small number of Si atoms (e.g., the near-surface region in Si nanocrystallites) exhibits the PL. \(^16\)

If we were to further examine the polarization properties of the PL, we could find that the PL has a character of strongly linear polarization. Its maximal intensity component appears in the direction perpendicular to the polarization direction of excitation light and its minimal component appears in the direction parallel to that of excitation light. This result can clearly be seen in the low-temperature (\(77\) K) PL spectra, as shown in Fig. 2, which are obtained with the vertical polarization direction of excitation light. The two low-temperature spectra clearly display composite band structures with large intensities. The maximal PL component appears in the horizontal polarization direction. If we change the vertical polarization direction of excitation light into the horizontal polarization direction, the maximal PL component appears in the vertical polarization direction. When using circularly polarized excitation light, no obvious PL polarization effect is observed in samples A and B. These results above indicate that the PL is closely related to the polarization direction of excitation light.

We define the degree of linear polarization \(\delta = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)\), where \(I_\parallel\) and \(I_\perp\) are the intensity components of the PL polarized parallel and perpendicular to the plane of polarization of the excitation light, respectively. From Fig. 2 we can plot the room-temperature and low-temperature \(\delta\) values of samples A and B as a function of emission wavelength, as shown in Fig. 3. The figure has the
following features: (1) The $\delta$ value can negatively reach $\sim90\%$ on the low-energy side. (2) The $\delta$ value changes with the sample. It generally has a larger value in the sample with a larger inhomogeneity.\(^{10}\) The difference caused by the sample inhomogeneity is small at room temperature and becomes obvious at low temperature. (3) The $\delta$ value tends to negatively increase with the wavelength of detected emission.

If we change the sample orientation ($\theta_{\text{Sample}}$) with respect to the direction of linear polarization of the excitation beam, the $\delta$ value hardly changes, as presented in Fig. 4 for sample B with $\theta_{\text{Sample}}=0^\circ$ and $90^\circ$. This result indicates that the polarization direction of the PL is independent of the crystallographic orientation of the sample. In addition, temperature dependence of the PL polarization retention is also a matter of interest, because it directly relates to the photoelectronic excitation and subsequent carrier transport in our samples. From Fig. 3, we can further find that for sample B, no appreciable difference between the room-temperature and low-temperature $\delta$ values was observed, indicating that the $\delta$ value from sample B hardly changes with the temperature. However, for sample A, a discrepancy between the room-temperature and low-temperature $\delta$ values is pronounced. If we select other illuminated spots on the sample surface to examine the linear polarization property of the PL, the same results can be obtained for samples A and B.

In PS, the linearly polarized property of the PL has been discussed thoroughly.\(^{3-6}\) The maximal polarization degree was observed to be about 30% on the high-energy side. In other nanostructural materials such as In\(_x\)Ga\(_{1-x}\)As quantum-well wires\(^{17}\) with widths between 10 nm and 1 $\mu$m, the polarization degree may reach about 60% (positive). Recently, it was reported that there exists a negative polarization degree of $\sim20\%$ in the PS film grown on a (100)-oriented $c$-Si substrate.\(^{6}\) It is not related to the polarization of the exciting light but depends on sample orientation. For our ML’s, the polarization degree $\delta$ can negatively reach $\sim90\%$. This result is reported for the first time to our knowledge. The strongly linear polarized PL is not due to the momentum alignment of photoexcited carriers because of the absence of polarization preservation in the case of the excitation by circularly polarized light.\(^{5}\) It also cannot originate from a selective population of conduction-band valleys caused by an excitation with linearly polarized light,\(^{18}\) because electrons simultaneously photoexcited into different valleys due to a halfway angle of the polarization direction with respect to the crystallographic axes recombine incoherently, which reduces the degree of polarization retention more than in the case where the polarization direction is properly aligned to the axes. As a result, $\delta$ should depend on the sample orientation to some extent for single crystal materials. However, our results indicate that the $\delta$ value from our ML’s has no sample orientation dependence. In addition, we cannot explain our results within a model of our ML’s as an aggregate of flattened and elongated ellipsoid Si:H nanocrystals embedded in an $a$-$Si:H$ dielectric matrix, because the PL polarization is not related to the sample orientation.\(^{6}\)

For our ML’s, Raman scattering\(^{5}\) has suggested the existence of the interfacial region between the $c$-$Si$ core and the $a$-$Si:H$ surface layer in the nc-$Si:H$ crystallites and the interfacial region was proposed to be responsible for the visible PL. Thus, a possible origin that can explain our experimental results can be presented on the basis of the three-region model.\(^{16}\) According to this model, the photogeneration of carriers occurs in the $c$-$Si$ core. Some of them transfer to the interfacial layer by a thermally activated diffusion process. The visible PL is then caused by the radiative recombination of carriers confined in the interfacial layer. The model can easily explain the PL intensity dependence and the PL peak energy independence on the size of the $c$-$Si$ core. The smaller the core, the higher the efficiency of carrier transfer from the core to the interface layer. Since the PL comes from the interfacial region, the quantum confinement in the $c$-$Si$ core does not affect the PL peak energy. According to the relation between the polarization degree and the PL efficiency, we believe that the PL efficiency reflects the structural homogeneity of a sample. A relatively inhomogeneous sample has a lower PL efficiency and thus a larger polarization degree. This conclusion is based on the experimental result of the electroluminescence from nc-$Si:H$ nanocrystals embedded in $a$-$Si:H$ films.\(^{15}\) Since sample A has more inhomogeneous structure than sample B,\(^{16}\) sample A displays a larger $\delta$ (negative) value than sample B.
The condition for carrier confinement is roughly determined by the relative magnitude of the band-gap energy of each region. For our nc-Si:H crystallites, the a-Si:H surface surrounding the nanocrystallites eliminates the weak/unstable Si-Si bonds through the etching effect of $\text{[H]}_{1}$ radicals and its band-gap energy of $\approx 2.0$ eV makes the photogenerated carriers confined within the c-Si core. According to the effective-mass theory, the band-gap energy of the core with a diameter less than 4 nm is larger than 2.0 eV. Theoretical calculations show that the energy gap of the interfacial layer is around 1.7 eV and lower than those of both the c-Si core and the outer surface, and increases with the terminated H concentration. Thus, the photogenerated carriers can be confined in the shell region. The coupling of confined carriers with local vibrations of the interfacial region is expected to increase with the confinement of carriers at the interfacial region. This can be seen from fine structures of the PL spectra. Figure 5 shows the low-temperature unpolarized PL spectra of samples A and B with fine structures, measured under the condition of no analyzer.

The three-region model can explain the anomalously linear polarized property of the visible PL from our ML's. Since the luminous sample of structural inhomogeneity has a variety of crystallites with different shapes and boundaries, these crystallites could induce an anisotropy in their electronic structure, and therefore their optical response, through a change in the position and/or the extension degrees of the localized wave functions of carriers within them. Therefore, the linearly polarized light preferentially excites the optically anisotropic crystallites such that they can respond to the excitation light with a large electronic transition probability. Linearly polarized PL occurs if the photoexcited carriers recombine just at the crystallites where they are generated. PL depolarization may occur if the carriers escape from one crystallite to another and recombine there. The negative polarization degree observed in our experiments indicates that the PL is preferentially polarized in the direction perpendicular to the polarization of the exciting light. Here we emphasize that the PL is caused by the confined carriers in the interfacial region rather than in the c-Si cores. Since the carrier transfer only exists within a crystallite, the $\delta$ value is basically independent of the temperature. This result is essentially true for sample B with a relatively homogeneous structure. However, for sample A with a relatively inhomogeneous structure, the discrepancy between the room-temperature and low-temperature $\delta$ values may mainly arise from large optical anisotropy of the nc-Si:H crystallites in the sample. For a luminous sample with large optical anisotropy degree and large crystallite sizes, potential fluctuation should be higher along the longitudinal direction of a nanocrystallite than that in the sample with small optical anisotropy degree and small crystallite sizes. Therefore, carrier transport from the core to the interfacial region will depend on the temperature to the same extent. In addition, relatively low PL intensity from sample A indicates that a small amount of photogenerated carriers may further transfer to the outer space and produce nonradiatively recombination on the surface defects and disordered states. This process for carrier transfer may also relate the $\delta$ value to the temperature.

The origin of the emission-wavelength dependence of $\delta$ is still unclear at present. To understand this point, we measured the PL spectra of samples A and B by using the 488-nm line of an Ar$^+$ laser as excitation source to examine the excitation-wavelength dependence of the $\delta$ value. Figure 6 shows the corresponding experimental results from samples A and B. It can be seen from Fig. 6 that for sample...
$B$, the $\delta$ value displays a small excitation-wavelength dependence. The shorter-wavelength excitation has a slightly larger $\delta$ value (negative). For sample A, this situation becomes pronounced. According to the experimental results above, a possible origin might be presented. Our ML sample consists of a great number of luminous nc-Si:H crystallites with disordered electronic boundaries. If we assume that in our sample some luminous crystallites that emit shorter-wavelength light have higher optical anisotropy, excitation of higher-energy PL generally needs higher-energy excitation light. In other words, shorter-wavelength excitation yields shorter-wavelength PL, which will then lead to a larger $\delta$ value (negative). Similarly, such a distribution of crystallites may also account for the small effect of the excitation wavelength on $\delta$. For this problem, further work is needed to clarify its essential mechanism.

In conclusion, we report strongly polarized PL from alternating nc-Si:H/α-Si:H ML's. The PL is almost linearly polarized in the direction perpendicular to the polarization of excitation light, independent of the sample orientation. The degree of linear polarization $\delta$ negatively increases with decreasing emission energy, reaching a maximum of $\sim90\%$ on the low-energy side, and different temperature dependence is observed. Since the obtained PL spectra show no crystallite size dependence of the peak energy and fine structures, we attribute these anomalous polarization properties to the radiative recombination of carriers confined in the interfacial region of optically anisotropic and randomly distributed Si:H nanocrystals.

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