Effect of nitride passivation on the visible photoluminescence from Si-nanocrystals

Moon-Seung Yang, Kwan-Sik Cho, Ji-Hong Jhe, Se-Young Seo, and Jung H. Shin
Department of Physics, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong, Yuseong-gu, Daejeon, Korea
Kyung Joong Kim and Dae Won Moon
Nano Surface Group, Korea Research Institute of Standards and Science (KRISS), P.O. Box 102, Yuseong-gu, Daejeon, Korea

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The effect of nitride passivation on the visible photoluminescence from nanocrystal Si (nc-Si) is investigated. Silicon-rich silicon nitride (SRSN) and silicon-rich silicon oxide (SRSO), which consist of nc-Si embedded in silicon nitride and silicon oxide, respectively, were prepared by reactive ultrahigh vacuum ion beam sputter deposition followed by a high temperature anneal. Both SRSN and SRSO display photoluminescence peaks after high temperature annealing, coincident with the formation of Si nanocrystals, and similar changes in the peak luminescence position with the excess Si content. However, the luminescence peak positions from SRSN are blueshifted by about 0.6 eV over that of comparable SRSO such that its luminescence peaks in the visible range. The results demonstrate that control of the surface passivation is critical in controlling the nc-Si luminescence, and indicate the possibility of using nitride-passivated nc-Si for visible luminescence applications including white luminescence. © 2004 American Institute of Physics.

Ever since the report of luminescence by Canham et al.,1 nanocrystal Si (nc-Si) has been the subject of intense research. In particular, silicon-rich silicon oxide (SRSO), which consists of nc-Si embedded inside an SiO2 matrix, has received particular attention due to its ability to produce robust, well-passivated nc-Si film in a manner that is compatible with the standard Si processing technologies.2 By now, efficient light-emitting diodes as well as the possibility of optical gain have been demonstrated using SRSO.3,4

However, the luminescence from nc-Si in SRSO was reported to peak only in the near-infrared range of 700–900 nm even when the size of nc-Si was controlled to below 2 nm.5,6 The few reports of visible luminescence reported from SRSO are usually attributed to oxide defects that disappear either upon high temperature annealing or hydrogenation.7–9 Recently there have been several reports10,11 that the luminescence from oxide-passivated nc-Si originates from oxygen-related deep surface states whose energy varies only weakly with nc-Si size, thereby explaining the difficulty of obtaining visible luminescence from SRSO even with nm-sized nc-Si with sufficiently strong quantum confinement effect.

Such results also imply, however, that with a different surface passivation scheme, visible luminescence from nc-Si is in principle possible. One such alternative is Si nitride. Si nitride is widely used in Si process, and is transparent to the visible light. It also has a band gap that is smaller than that of SiO2, facilitating carrier injection for optoelectronic application. There have been scattered reports on photoluminescence from nitride passivation of nc-Si,12–14 but the luminescence was still centered in the near-infrared range. Visible luminescence has been reported from nitride passivated amorphous nano-Si formed by low temperature deposition of a-Si:H:N.15,16 However, it is not clear that such results can be translated directly to luminescence from nano-crystalline Si. Furthermore, a-Si:H:N matrix itself can luminesce in the visible range,17 complicating the analysis.

In this letter, we investigate the effect of nitride passivation on the visible luminescence from nc-Si by comparing the photoluminescence properties of similarly prepared silicon-rich silicon nitride (SRSN), which consists of nc-Si embedded inside a nitride matrix, and silicon-rich silicon oxide, which consists of nc-Si embedded inside an oxide matrix. We find that both SRSN and SRSO display photoluminescence peaks after high temperature annealing, coincident with the formation of Si nanocrystals, and that the luminescence peak position can be controlled by controlling the excess Si content. However, the luminescence peak positions from SRSN are blueshifted by 0.6 eV over that of comparable SRSO such that its luminescence peaks in the visible range in which SRSO does not show any luminescence. The results demonstrate that control of the surface passivation is critical in tuning the nc-Si luminescence, and indicate the possibility of using nitride-passivated nc-Si for visible luminescence applications including white luminescence.

SRSO thin films were grown by ion beam sputter deposition of a Si wafer with Ar ions under O2 gas flow using a Kaufman-type dc ion gun. However, SRSN thin films were deposited by using N2 ions as sputtering ions. The base-pressure was 2.0 × 10−8 Torr, and the ion energy was 750 eV. The stoichiometry of the deposited films was controlled by varying the reactant gas flow, and analyzed with in situ x-ray photoelectron spectroscopy using the Al Kα line of 1486.6 eV and relative sensitivity factor calibrated with Rutherford backscattering spectroscopy. The excess Si content of the films, Siex, defined as the Si content in excess of the stoichiometric Si12N14 and SiO25,8 ranged from 6 to 12 at. % and 3 to 11 at. % for SRSN and SRSO, respectively. After

aElectronic mail: jhs@mail.kaist.ac.kr

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deposition, the films were furnace-annealed in a flowing N₂ environment, and subsequently hydrogenated by a 1 h anneal at 650 °C in forming gas. In all cases, ultrahigh purity gases were used. Photoluminescence (PL) spectra were measured at room temperature using the 325 nm line of He–Cd laser and a charge coupled device camera. The pump power was 40 mW, and all spectra are corrected for the system response.

Figure 1 shows the anneal temperature dependence of the PL spectrum from the SRSN film with Si\textsubscript{ex} of 8 at. % after isochronal anneals of 10 min. An anneal time of 10 min was chosen because the increase in the PL intensity saturated after an anneal time of 10 min (data not shown). No PL could be observed from as-deposited films. Visible PL emerges upon high temperature annealing. The PL intensity tends to increase with increasing annealing temperature. Among the anneal temperatures investigated, 950 °C resulted in the highest PL intensity. Previously, it has been reported that annealing SRSN films at 950 °C initiates formation of nc-Si.\textsuperscript{14} Such formation of nc-Si in our SRSN films after 950 °C anneal is confirmed by high-resolution transmission electron microscopy, as shown in the inset.

Figure 2 shows the effect of hydrogenation on the PL spectra. In all cases, we observe a slight increase in the PL intensity. On the other hand, we did not observe any changes in the overall PL spectra shape.

In the case of SRSO, all films were annealed for 20 min at 1100 °C and hydrogenation, as investigations into the effect of preparation conditions have shown this to result in the optimum nc-Si luminescence from SRSO, in agreement with previously reported results (data not shown).\textsuperscript{6}

Figure 3 compares the PL spectra of the similarly prepared SRSO and SRSN films. We observe broad luminescence peaks from all films. Furthermore, both SRSN and SRSO films show systematic blueshift of the luminescence with decreasing Si content. The dependence of the luminescence peak position and intensity on the excess Si content is shown in the inset.

Compared to SRSO, there is comparatively little investigation into the SRSN luminescence. However, when taken together, the data shown in figures can be explained consistently by assigning it to nitride-passivated nc-Si. First, high temperature anneals in excess of 950 °C and resultant removal of defects and precipitation of nc-Si are necessary to obtain strong SRSN luminescence. Second, hydrogenation increases the SRSN PL intensity without any changes in the spectrum shape. This is in contrast to the previously reported effect of hydrogenation on defect luminescence, which either completely quenches the defect luminescence\textsuperscript{7,8} or changes the PL spectrum completely due to the modification of the mid-gap states.\textsuperscript{17} Finally, the effect of varying the Si content on the PL properties of SRSO and SRSN films is remarkably similar. As summarized in the inset to Fig. 3, both show a systematic blueshift of about 17% with the decreasing Si\textsubscript{ex}. And both show maximum PL intensity near the excess Si content of about 8–10 at. %, and a strong reduction in the PL intensity with further decrease in the excess Si content even though the films are not yet fully stoichiometric, and thus contain defects.

The important difference, however, is that compared to SRSO luminescence, the SRSN luminescence is shifted by about 0.6 eV such that it peaks in the visible range, where SRSO does not show any luminescence. We attribute such shift to the effect of nitride passivation. Pužder et al. have shown that the main reason for the oxygen-induced reduction of the nc-Si band gap is not the presence of oxygen per se but the distortion of the local $sp^3$ network by double-bonded oxygen.\textsuperscript{11} Such distortion of $sp^3$ network, however, would be inevitable for oxide-passivated nc-Si, since there exists...
strong strain at the Si/SiO2 interface. On the other hand, we have recently shown that nitrogen can eliminate the strain at the Si/SiO2 interface nearly completely. As there is a good correlation between the degree of the sp³ network distortion and the reduction in the nc-Si band gap, such elimination of strain by nitrogen passivation should result in increased nc-Si band gap, as is observed.

Furthermore, the ability to control luminescence peak position with composition opens up the possibility of integrating different color emitter on a single chip using a single anneal step. This is demonstrated in Fig. 4, which shows the PL spectrum of a SRSN film composed of multiple, 20 nm thin layers with 6–12 at. % excess Si. We observe a broad PL peak with a full width at half maximum of 1 eV covering the entire visible range, resulting in slightly greenish white luminescence with the CIE coordinates of x=0.4 and y=0.42.

In conclusion, we have investigated the luminescence from silicon-rich silicon nitride. We observe visible luminescence whose peak luminescence position can be controlled by varying the excess Si content. Based on a comparison with silicon-rich silicon oxide, we attribute the luminescence to nc-Si whose band gap is wider than that of oxide-passivated nc-Si due to nitride passivation of the nc-Si surface.

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