Activation of luminescence in polycrystalline silicon thin films by ultrasound treatment

J. Koshka and S. Ostapenko[a]
Center for Microelectronics Research, University of South Florida, Tampa, Florida 33620

T. Ruf and J. M. Zhang
Max-Planck-Institut für Festkorperforschung, Stuttgart D-70569, Germany

A dramatic increase of infrared photoluminescence (PL) intensity by a factor of 2 orders of magnitude is observed after a few minutes at 250 °C of ultrasound treatment (UST) applied to polycrystalline silicon thin films on glass substrates. In films obtained by solid-phase crystallization of amorphous silicon at 550 °C, UST enhances the PL band intensity at 0.7 eV, and also activates a new luminescence maximum at about 0.9 eV. We prove that the 0.9 eV PL band is related to the amorphous fraction of poly-Si films. Due to similarities in spectral shape and temperature behavior, this UST activated luminescence is attributed to a ''defect'' PL band previously observed in hydrogenated amorphous Si. This conclusion is confirmed by using a set of films with controlled fractions of the amorphous to crystalline phase. A mechanism of ultrasound stimulated hydrogen detrapping followed by hydrogen diffusion and passivation of nonradiative centers (e.g., dangling bonds) in polycrystalline and amorphous Si films is discussed. © *1996 American Institute of Physics.* [S0003-6951(96)01143-6]

High performance thin film silicon based transistors are the key elements for flat-panel active-matrix liquid-crystal display technology. Hydrogenated amorphous (α-Si) and fine grain polycrystalline silicon (poly-Si) films on glass are materials for thin-film transistors.[1] Operational parameters of both α-Si and poly-Si transistors are affected by a high density of localized states (predominantly Si dangling bonds) at the interface with the gate oxide and in the bulk. A conventional approach to reduce a density of these states is the passivation of thin films with atomic hydrogen. The hydrogen diffusivity in poly-Si and α-Si is described by an activation energy of 1.3–1.5 eV and is recognized as a trap-limited process,[2,3] with a diffusion coefficient given by

$$D_{\text{H}} = D_{\text{H}_0^*}(N_i/N_t) = D_0 \exp(-E_0/kT)$$
$$\times \exp(-\Delta E/kT), \qquad (1)$$

where D_{H_0} is the hydrogen diffusivity in crystalline Si with an activation energy $E_0 = 0.48$ eV, N_i/N_t is a fraction of interstitial to trapped hydrogen, and ΔE is a binding energy of trapped atomic hydrogen. As a consequence of hydrogen trapping, a conventional plasma hydrogenation processing of poly-Si requires several hours at 350 °C.[4]

It was recently observed that low-temperature ($T < 100$ °C) ultrasound treatment (UST) applied to plasma hydrogenated poly-Si thin films causes an enhancement of the hydrogenation process.[5] It was documented that both transport and recombination properties of plasma hydrogenated poly-Si can be noticeably improved by UST. The utility of UST processing to reduce a leakage current and to shift a threshold voltage in commercial hydrogenated poly-Si thin film transistors was demonstrated.[6] A new mechanism of UST enhanced liberation of atomic hydrogen from an electrically nonactive state (''reservoir'') and following passivation of dangling bonds has been suggested.[5,6] In this letter we

report on a strong influence of UST processing at temperatures up to 280 °C on the photoluminescence (PL) efficiency of poly-Si films.

Semi-insulating undoped low-pressure chemical vapor deposition (LPCVD) amorphous Si films with a thickness of about 0.5 μm were deposited at 550 °C on glass substrates (Corning 7059). The films were annealed at 550 °C in a nitrogen flow to develop a crystalline structure with predominant $\langle 111 \rangle$ orientation. Using annealing time from 8 to 75 h, a set of samples with a different fraction of crystalline to amorphous phases was designed. Raman spectra of thermally recrystallized films enabled us to determine this fraction from the intensity ratio of the crystalline peak at 520 cm^{-1} to the amorphous peak at about 480 cm^{-1} using a procedure described in Ref. 7. Raman measurements were done at room temperature with 457.9 nm laser excitation under a microscope. Poly-Si films obtained by excimer laser recrystallization of α-Si as well as films deposited at 625 °C were also investigated. Only one Raman peak at 520 cm^{-1} due to poly-Si was observed, which proves a high level of crystallinity in both previous cases. PL spectra at 4.2–300 K were analyzed using a SPEX 500 M spectrometer coupled with cooled Ge or a PbS photodetector and lock-in amplifier. PL spectra were corrected for a setup spectral response. An Ar$^+$ laser 514 nm line with power from 30 to 80 mW was used as a PL excitation source. Special precautions were taken to avoid an error in PL intensity measurements due to removing and repositioning the same sample at the holder after UST. A reproducibility of sample positioning was 0.5 mm yielding an accuracy of PL intensity reading better than 5%.

For UST experiments, ultrasound vibrations were generated in poly-Si or α-Si films through a glass substrate using a circular 75-mm-diam piezoelectric transducer (PZT-5A). For good acoustic contact, the sample was pressed against a transducer front surface with a spring. The UST transducer was operated at resonance of its radial vibrations of 25 kHz.

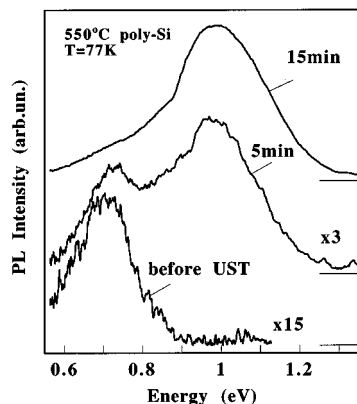[a]Electronic mail: ostapenk@cmd.usf.edu

FIG. 1. PL spectra of 550 °C annealed poly-Si films (24 h) before and after two consecutive UST exposures of 5 and 15 min at 250 °C.
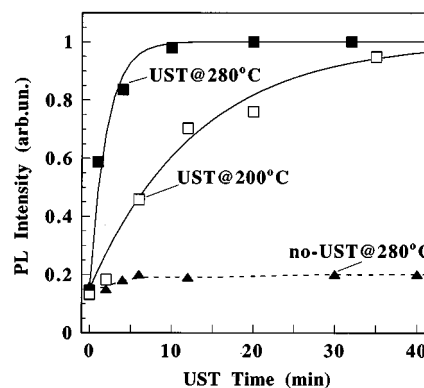

FIG. 2. Isothermal UST kinetics of the 0.9 eV PL band (points) and single-exponential fit (solid). Control sample was held at 280 °C and had no UST processing.

The amplitude of sample vibrations in acoustic contact with the transducer was monitored *in situ* by a calibrated contact acoustic probe. The maximum acoustic strain amplitude on the film surface was of the order of 10^{-5}. The temperature of the sample under UST was stabilized from 50 to 280 °C and measured by a thermocouple attached to the film surface. The upper UST temperature was limited due to degradation of the piezoelectric transducer. UST at elevated temperatures was performed in nitrogen ambient with a rate of N_2 flow of 5 ℓ/min. A control sample from the sample poly-Si wafer was kept without ultrasound treatment at exactly the same temperature to separate a possible effect of thermal processing.

The PL spectrum of thermally recrystallized poly-Si thin films is dominated by a deep infrared band at 0.7 eV and a half-width of 170 meV (Fig. 1). Luminescence intensity of as-deposited films was lower than the sensitivity limit of PL setup. By increasing the recrystallization time of 550 °C films to 75 h, we found that the intensity of the 0.7 eV PL band monotonously increases by a factor of 10 in 75 h annealed samples compared to 8–12 h annealed films. A similar PL band ($h\nu_{max} = 0.68$ eV) was observed previously in Cz–Si wafers thermally annealed for 64 h at 450 °C, and was attributed to the generation of oxygen precipitates in silicon.[8] Our poly-Si samples were annealed under very similar conditions (75 h at 550 °C). Therefore, the intensity of 0.7 eV band can be used to monitor changes of recombination properties in the poly-Si phase of films.

After UST was applied to 550 °C annealed films at $T_{UST} = 150$–280 °C, we observed two noticeable changes in the PL spectrum (Fig. 1). The first is the increase of the 0.7 eV band intensity by a factor of 2–4 (in different samples), which is consistent with data of low-temperature UST processing of hydrogenated poly-Si films.[5] The second effect is a strong UST activation of a ''new'' broad PL band with a maximum at 0.92–0.98 eV and a half-width of 260 meV at 77 K (referred to hereafter as the 0.9 eV band). We noticed that a dramatic enhancement of the 0.9 eV band exceeding *two* orders of magnitude compared to untreated sample requires only a few minutes of UST processing performed at 250–280 °C. After UST activation of luminescence is completed (5 min at 280 °C), the PL spectrum is entirely dominated by the 0.9 eV band (Fig. 1).

UST processing was performed at different temperatures between 150 and 280 °C. Corresponding points of isothermal kinetics of the 0.9 eV band at two temperatures and their single-exponential fits are shown in Fig. 2. For comparison, this picture also comprises PL kinetics of the control sample annealed without UST at 280 °C, which proves that the effect of 0.9 eV band activation is entirely UST related. The UST kinetic is characterized by a time constant of 3 min at 280 °C that increases to 25 min at 150 °C. From the Arrhenius plot of the UST time constant we find the UST activation energy to be $E_{UST} = 0.33 \pm 0.05$ eV.

We have strong arguments that the UST activated 0.9 eV band is related to the residual amorphous phase of recrystallized poly-Si films. The saturated intensity of the 0.9 eV band after completion of UST processing is a function of 550 °C annealing time and therefore depends on a fraction of the α-Si phase in the films. Raman spectroscopy reveals a clear trend of an increase of the polycrystalline fraction with 550 °C annealing time as shown in Fig. 3. It was found that the 0.9 eV band has a maximum intensity in films with a significant fraction of the α-Si phase, and it gradually decreases to a negligible value in films where the poly-Si phase dominates (inset in Fig. 3). We noticed that the UST effect is
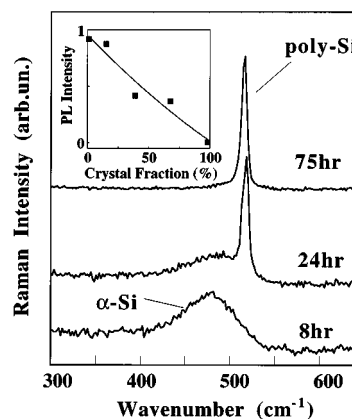

FIG. 3. Raman spectra at 550 °C LPCVD films vs 550 °C annealing time. Maximum at 520 cm^{-1} corresponds to the crystalline phase; the band at 480 cm^{-1} is due to the α-Si phase. Inset: Dependence of 0.9 eV PL band saturated intensity vs a fraction of the crystalline phase in films.

TABLE I. Parameters of UST activated PL band in 550 °C poly-Si and ''defect'' luminescence in hydrogenated α-Si (Ref. 9).

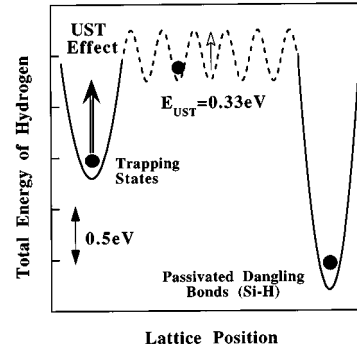|	UST activated poly-Si	Hydrogenated α-Si
PL maximum (eV)	0.92–0.98	0.9
Half-width of PL band (meV)	280–300	350
Activation energy of temperature quenching (meV)	120	80–100

FIG. 4. Model of UST enhanced hydrogenation in poly-Si and α-Si films. The energy scale corresponds to values in Ref. 15. Ultrasound promotes liberation of H trapped at grain boundary defects. This is followed by interstitial diffusion of atomic hydrogen, and the capturing at dangling bonds. Notice that UST activation energy (0.33 eV) is very close to that of hydrogen diffusivity in crystalline Si (about 0.5 eV).

also negligible in films either deposited at 625 °C or recrystallized using an excimer laser; these films are entirely crystalline according to Raman spectra. Furthermore, a parameters of the 0.9 eV band are very close to a ''defect'' PL band previously observed in hydrogenated α-Si films.[9] In Table I we compared maximum position, $h\nu_{max}$, and the PL half-width as well as the activation energy of temperature quenching of both bands.

It was shown previously that UST applied to plasma hydrogenated poly-Si films can activate the atomic hydrogen from an electrically nonactive state.[5,6] It is also known that in LPCVD films obtained by the low-temperature decomposition of silane (SiH_4), hydrogen is incorporated in as-grown amorphous films.[10] Therefore, two different hydrogen mediated mechanisms can account for the observed UST effects: (a) UST creation of radiative recombination centers (e.g., due to their dehydrogenation) and (b) UST stimulated hydrogen detrapping followed by a hydrogen diffusion and passivation of nonradiative centers, like dangling bonds and interface defects. To eliminate this ambiguity we performed prolonged annealing of 550 °C films in a forming gas containing 5% H_2 in nitrogen, which is known to introduce hydrogen in poly-Si films. The 0.9 eV PL band was clearly observed after 2 h at 300 °C forming gas annealing, while similar annealing of a control sample in N_2 ambience did not show any PL activation. This experiment rules out option (a) and proves a hydrogen relation of the UST effect on PL enhancement.

A model of UST activated hydrogenation of nonradiative centers (e.g., dangling bonds) is illustrated in Fig. 4. After film deposition and 550 °C anneal the hydrogen is partially trapped at grain boundary defects, but there is a substantial number of nonsaturated dangling bonds. It was suggested that hydrogen molecules (H_2 or H_2^*) can be responsible for H trapping in poly-Si.[11] Alternatively, a strained Si–Si bond-center position near grain boundaries is another hydrogen bound state.[12] Regarding the α-Si phase, hydrogen can be loosely bound in weak Si–Si bonds[3] or reside in clusters.[13] We postulate that UST promotes a release of hydrogen from traps. This process corresponds to a reduction of the hydrogen binding energy ΔE in Eq. (1). A physical reason for such UST induced hydrogen detrapping is a selective absorption of ultrasound by grain boundaries, dislocations, voids, and other extended crystal defects where hydrogen can reside. Being liberated from traps, hydrogen will diffuse with the diffusion coefficient of crystalline Si (Ref. 14): $D_H = 9.4 \times 10^{-3*} \exp(-0.48 \text{ eV}/kT)$ (cm^2/s).

The UST activation energy ($E_{UST} = 0.33 \pm 0.05$ eV) has a value close to the activation of H diffusion. A possible reduction of this energy can be attributed to UST stimulated

diffusion of hydrogen similar to Cr_i in Cz–Si.[16] The diffusion length for H migration under UST ($T_{UST} = 280$ °C, $\Delta t = 3$ min) can be estimated as $L = (D_H \Delta t)^{1/2} = 76$ μm. This value substantially exceeds the 100 nm grain size of poly-Si films, which explains why liberated hydrogen atoms can quickly approach nonradiative centers in poly-Si and α-Si phases.

We suggest that the UST effect is beneficial to both hydrogenated poly-Si and α-Si:H films on glass, where hydrogen binding and transport can be altered by ultrasound to design films with optimal parameters.

[1] J. S. Im and R. S. Sposili, Mater. Res. Bull. **21**, 39 (1996),

[2] W. B. Jackson, N. M. Johnson, C. C. Tsai, I.-W. Wu, A. Chiang, and D. Smith, Appl. Phys. Lett. **61**, 1670 (1992).

[3] R. A. Street, Physica B **170**, 69 (1991).

[4] N. H. Nickel, N. M. Johnson, and C. G. Van de Walle, Phys. Rev. Lett. **73**, 3393 (1994).

[5] S. Ostapenko, L. Jastrzebski, J. Lagowski, and R. K. Smeltzer, Appl. Phys. Lett. **68**, 2873 (1996).

[6] S. Ostapenko, L. Jastrzebski, J. Lagowski, and R. K. Smeltzer, Proceedings of the MRS Meeting, San Francisco, 1996 (unpublished).

[7] H. Kakinuma, M. Mohri, M. Sakamoto, and T. Tsuruoka, J. Appl. Phys. **70**, 7373 (1991).

[8] M. Tajima, J. Cryst. Growth **103**, 1 (1990).

[9] R. A. Street, Adv. Phys. **30**, 593 (1981).

[10] T. Kamins, *Polycrystalline Silicon for Integrated Circuit Applications* (Kluwer Academic, Norwell, MA, 1988), p. 84.

[11] N. H. Nickel, N. M. Johnson, and W. B. Jackson, Appl. Phys. Lett. **62**, 3285 (1993).

[12] C. G. Van de Walle and N. H. Nickel, Phys. Rev. B **51**, 2636 (1995).

[13] W. B. Jackson, P. V. Santos, and C. C. Tsai, Phys. Rev. B **47**, 9993 (1993).

[14] A. Van Wieringen and N. Warmoltz, Physica **22**, 849 (1956).

[15] C. G. Van de Walle, Phys. Rev. B **49**, 4579 (1994).

[16] R. Bell, S. Ostapenko, and J. Lagowski, *Defect and Impurity Engineered Semiconductors and Devices* (Materials Research Society, Pittsburgh, PA, 1995), p. 647.