MECHANISM OF ULTRASONIC ENHANCED HYDROGENATION
IN POLY-Si THIN FILMS

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Abstract. Ultrasound treatment (UST) was applied to improve electronic properties of polycrystalline silicon (poly-Si) films on glass. A strong decrease of sheet resistance by a factor of two orders of magnitude was observed in hydrogenated films at UST temperatures lower than 100°C. The UST effect is accompanied by improvement of a film electrical and optical homogeneity as confirmed by spatially resolved photoluminescence (PL) study. By applying UST at higher temperatures up to 280°C, a dramatic increase of infra-red photoluminescence (PL) intensity is observed in films obtained by solid-phase crystallization of amorphous silicon. UST enhances the PL band at 0.7eV, and also stimulates a new luminescence maximum at about 0.9eV related to the amorphous fraction of poly-Si films. Activation energy of the UST effect is 0.33eV. A new mechanism of ultrasonic stimulated hydrogen detrapping followed by a fast hydrogen diffusion and passivation of non-radiative centers in polycrystalline and amorphous Si films is suggested.

Introduction.

Poly-Si thin films on glass are promising materials for thin film transistor in active matrix liquid crystal displays and a new generation of thin-film solar cells. Compared with transistors using hydrogenated amorphous silicon (α-Si) films, poly-Si transistors have improved operational parameters due to a substantially higher electron mobility. However, grain boundary and interface defects in poly-Si lead to high off-state current and affect threshold voltage. A conventional approach to passivate these defect states and to reduce inter-grain barriers for electron transport is hydrogenation. Plasma hydrogenation using radio frequency or electron cyclotron resonance technique was proven to be effective to improve transport properties of poly-Si. The hydrogen defect passivation occurs in two steps: plasma penetration and a subsequent atomic hydrogen diffusion. The diffusion of hydrogen in poly-Si is slow compared with single crystal silicon due to a trapping at grain boundaries [1], typically resulting in a long hydrogenation time and electrical inhomogeneity within passivated regions of poly-Si. The trap-limited hydrogen diffusivity in poly-Si films is described by an activation energy of 1.3 to 1.5eV with a diffusion coefficient given by

$$D_H = D_{ho} \times (N_i/N_t) = D_o exp(-E_o/kT) \times exp(- \Delta E/kT) \tag{1}$$

where D_{Ho} is the hydrogen diffusivity in crystalline Si with an activation energy E_o=0.48eV; N_i/N_t is a fraction of interstitial to trapped hydrogen; and ΔE is a binding energy of trapped atomic hydrogen of the order of 1eV [2]. A suppression of hydrogen trapping can enhance the passivation of defect states to benefit transport properties of hydrogenated poly-Si films.

A new approach to enhance hydrogenation efficiency using the Ultrasound Treatment (UST) was reported recently [3]. Defect engineering using the method of UST was proven to be extremely beneficial in polycrystalline materials where ultrasound vibrations enhance an interaction between extended lattice defects, like grain boundaries and dislocations, with mobile point defects [4]. It was reported that the atomic hydrogen is a specifically suitable object for ultrasound stimulated defect reactions in poly-Si thin films [3,5]. In this paper, key experiments of the UST enhanced

hydrogenation are reviewed, and a new mechanism of UST stimulated hydrogen detrapping discussed.

Samples and experimental.

Semi-insulating silicon films with thickness of 0.3 to 0.5μm were deposited at 625°C and 550°C on Corning 7059 glass by low pressure chemical vapor deposition. The 625°C films had a crystallite structure with the average grain-size of 100nm, while the films deposited at 550°C were amorphous. The α-Si films were annealed at 550°C in a nitrogen flow to develop <111> oriented crystalline structure. Using annealing time from 8 to 75 hours, a set of samples with a different fraction of crystalline to amorphous phases was designed. Raman spectra of thermally recrystallized films enabled to determine this fraction from the intensity ratio of the crystalline peak at 520cm^{-1} to amorphous peak at about 480cm^{-1}. Poly-Si films were also obtained by eximer laser recrystallization of α-Si and compared to films deposited at 625°C. Only one Raman peak at 520cm^{-1} due to poly-Si was observed, which proves a high level of crystallinity in both previous cases. The poly-Si films were selectively plasma hydrogenated using a pattern defined by an opening in an Al mask. This enabled us to study UST effects by comparing hydrogenated with non-hydrogenated areas on the same film. The hydrogenation was performed at 300°C in a parallel plate RF plasma system operating at a 100ccm H$_2$ flow with 0.3Torr pressure and 200W radio frequency power or using a low pressure electron cyclotron resonance (ECR) plasma system.

For UST experiments, ultrasonic vibrations were generated in poly-Si films through a glass substrate using a circular piezoelectric transducer (PZT-5A). For good acoustic contact, a sample was pressed against a transducer front surface using a spring or vacuum contact. UST transducers operated at resonance frequency of radial vibrations of 25KHz or 70KHz. 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 a film surface was of the order of 10^{-3}.

Temperature of a sample under UST was stabilized from 50°C to 280°C and measured by a thermocouple attached to the film surface. The upper UST temperature was limited by a Curie point of the piezoelectric transducer. UST processing at elevated temperatures was performed in nitrogen ambient with a rate of N$_2$ flow of 5 l/min. A control sample from the same poly-Si wafer was kept without ultrasound at exactly the same temperature to separate a possible effect of thermal processing on material properties. Detail parameters and operational principles of automatic UST station can be found in [6].

The UST effect was monitored by measurements of sheet resistance at room temperature using the four-point-probe method. Concurrently, spatially resolved photoluminescence (PL) and nano-scale contact potential difference (CPD) mapping were performed. Details of CPD method using atomic force microscope are published elsewhere [4]. Photoluminescence at 4.2 to 300K was analyzed using a SPEX 500M spectrometer coupled with cooled Ge or PbS detector. An Ar$^+$-laser 514nm line with power from 30 to 80 mW was used as a PL excitation source.

Results.

Plasma hydrogenation applied to poly-Si films reduces resistance by a factor of one order of magnitude due to increased electron mobility after passivation of grain-boundary defects.

A decreased resistance is saturated to a minimum value of the order of 10^9 Ω/sq after 3 to 5hr RF plasma processing of 0.35μm films. In the films where the plasma hydrogenation process was not completed, we observed the additional dramatic reduction of sheet resistance by a factor of *two orders* of magnitude after UST as shown in Fig. 1. Resistance in non-hydrogenated region was practically not changed after the UST. Notice, that UST-induced reduction of sheet resistance occurs at temperatures lower than 100°C, which is specifically beneficial for large scale poly-Si transistor applications requiring low-cost substrates with low thermal stability.

Another feature of the UST effect is reveled by the resistance distribution within the same poly-Si film. In Figure 1, the UST induced change of resistance in two regions of the same hydrogenated film is presented. Initially, a more than one order of magnitude variation in resistance was reduced to approximately 10% after a few consecutive steps of UST.
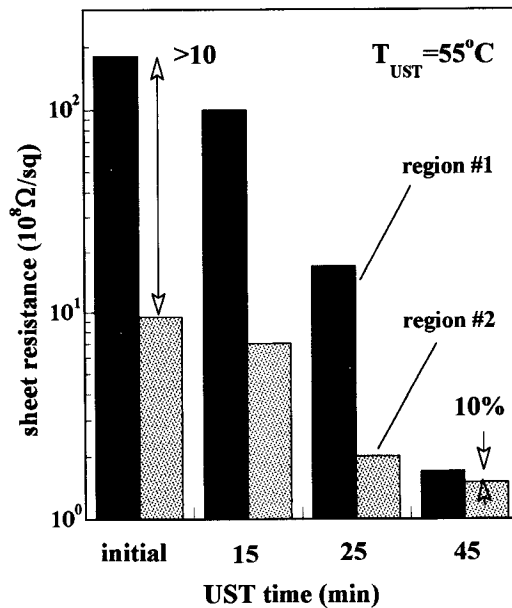

Fig.1 UST reduces resistance in hydrogenated poly-Si films due to improved passivation of dangling bonds.

Based on these findings, it was suggested that ultrasound vibrations applied to hydrogenated films can promote the process of defect passivation with atomic hydrogen. This statement is justified by the following spatially resolved PL study, and directly observed using nano-scale contact-potential difference mapping [3].

It was reported that PL spectroscopy allows defect monitoring in poly-Si films, and is specifically sensitive to the state of film hydrogenation [7]. At 4.2K the band-tail recombination dominates in PL spectrum of films deposited at 625°C. With increasing temperature, the band-tail luminescence is strongly quenched and deep 0.7eV PL band is retained and persists at room temperature.
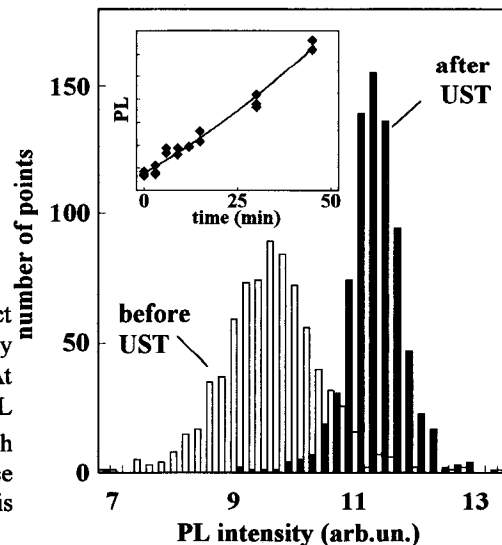

Fig.2 UST increases PL intensity and improves homogeneity of PL mapping due to redistribution of the hydrogen.

A similar PL band (hv_{max}=0.68eV) was observed previously in Cz-Si thermally annealed for 64hr at 450°C, and attributed to oxygen precipitates [7]. Notice, that our poly-Si samples were annealed under very similar conditions (75hr at 550°C). The intensity of 0.7eV PL band was used to monitor the UST effect on improvement of recombination properties of poly-Si. The increase of 0.7eV PL band intensity versus ECR plasma hydrogenation time is shown in Fig. 2 (insert). The PL increase occurs due to hydrogen passivation of non-radiative recombination centers at grain boundaries [7]. PL mapping technique with resolution of 100μm was applied to monitor a distribution of recombination centers and changes after UST. The results are presented in Figure 2 as two PL histograms of exactly the same hydrogenated film area prior to and immediately after the UST performed at 80°C for 1hr. The average PL intensity after UST exhibits an additional 25-30% increase and also narrowing by a factor of two of the half-width of the PL histogram. This result is consistent with UST improvement of resistance homogeneity shown in Figure 1.

It was assumed the UST is a thermally activated process which can be substantially facilitated at temperatures above 100°C. To verify this, thermally recrystallized at 550°C poly-Si films were subjected to UST at temperature up to 280^{0}C [5].

The PL spectrum of poly-Si thin films at 77 K is dominated by "oxygen" related band at 0.7eV (Fig. 3). Luminescence intensity of as-deposited films was lower than sensitivity limit of PL set-up. By increasing annealing time of 550°C films up to 75 hours, it was found that the intensity of 0.7eV band monotonously increases by a factor of ten in 75hr annealed samples compared to 8-12hr annealed films. Therefore, the intensity of 0.7eV band can be used to monitor changes of recombination properties in the poly-Si phase of films.
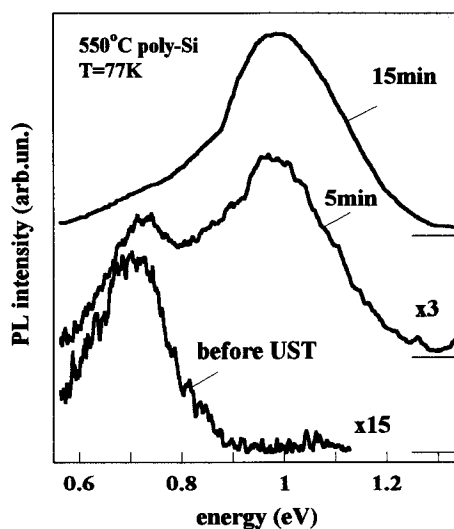

Fig.3 UST activation of 0.9eV PL band in α-Si phase of thin films: T_{UST} =250°C.

After UST was applied at T_{UST}=150-280°C, two noticeable changes in PL spectrum were observed (Fig. 3). The first is the increase of the 0.7eV band intensity by a factor of 2 to 4 in different samples, which is consistent with data of low-temperature UST processing of hydrogenated poly-Si films (Fig.2). The second effect is a strong UST activation of a "new" broad PL band with a maximum at 0.92 - 0.98eV and half-width of 260meV at 77K (referred hereupon as 0.9eV band). We notice that a dramatic enhancement of 0.9eV 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 (5min @280°C), the PL spectrum is entirely dominated by the 0.9eV band (Fig. 3).

UST processing was performed at different temperatures between 150 and 280°C. Corresponding points of isothermal kinetics of the 0.9eV band at two temperatures and their single-exponential fits are shown in Figure 4. For a comparison, the picture also comprises PL kinetics of a control sample annealed without UST at 280°C, which proves that the effect of 0.9eV band activation is entirely UST related. The UST kinetic is characterized by a time constant of 3min at 280°C which increases to 25min at 150°C. From the Arrhenius plot of UST time constant we find the UST activation energy: $E_{UST}=0.33$ +/- 0.05eV.

We have strong arguments that UST activated 0.9eV band is related to a residual amorphous phase of recrystallized poly-Si films.
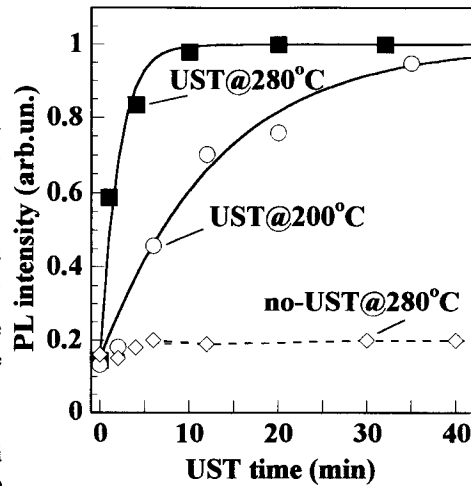

Fig.4. Isothermal UST kinetics of 0.9eV band activation (points), and exponential fit (solid).

The saturated intensity of the 0.9eV band after completion of UST processing is a function of 550°C annealing time, and therefore, depends on a fraction of α-Si phase in the films as proved by Raman spectroscopy: the 0.9eV band has a maximum intensity in films with significant fraction of α-Si phase, and is gradually decreased in films where the poly-Si phase is dominating. The UST activation of 0.9eV band is also negligible in poly-Si films either deposited at 625°C or recrystallized using an eximer laser. Furthermore, parameters of 0.9eV band are very close to a "defect" PL band previously observed in hydrogenated α-Si films [9]. We conclude, that UST promotes a passivation of non-radiative centers in the α-Si phase of recrystallized films.
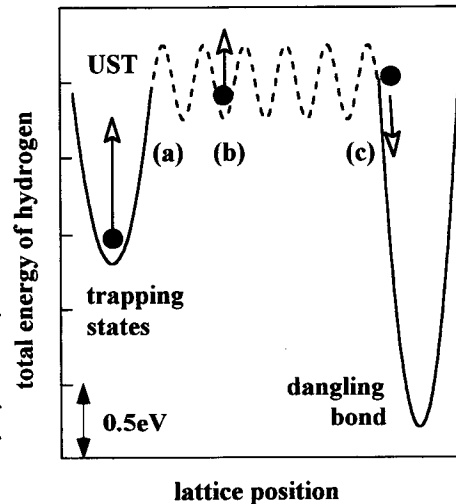

Fig.5. The model of UST enhanced hydrogenation in poly-Si and α-Si thin films.

Discussion: UST mechanism.

It is known that after plasma hydrogenation the total hydrogen concentration in poly-Si films can exceed the number of non-passivated dangling bonds by as much as two orders of magnitude [10]. In 550°C LPCVD films obtained by decomposition of silane (SiH_4) and annealing at 550°C, the concentration of trapped residual hydrogen can approach 10%. Therefore, a significant reservoir of trapped electrically non-active hydrogen is available in UST processed films to accomplish a defect passivation.

It is suggested that UST enhances the hydrogenation in a three-step mechanism schematically shown in Fig. 5: (a) UST hydrogen releasing from trapping states, (b) fast H-diffusion, and (c) hydrogen capture at dangling bonds. It is obvious that UST promotes a release of hydrogen from traps by a reduction of the hydrogen binding energy ΔE defined in Eq. (1). A physical reason of such UST induced hydrogen detrapping is a selective absorption of the ultrasound by grain boundaries and other extended crystal defects where hydrogen can reside. Being liberated from traps, hydrogen will diffuse with the diffusion coefficient of crystalline Si: $D_H = 9.4 \cdot 10^{-3} \times \exp(-0.48eV/kT)$ [cm^2/sec]. The UST activation energy 0.33eV is close to activation of H diffusion in silicon (0.48eV). A possible reduction of this energy can be attributed to UST stimulated diffusion of hydrogen [4]. The diffusion length of H migration under UST ($T_{ust}=280^{o}C$, $\Delta t=3min$) can be estimated as $L=(D_H \cdot \Delta t)^{1/2}=76\mu m$. This value substantially exceeds a 100nm grain-size of poly-Si films, which explains why liberated hydrogen atoms can quickly approach non-radiative centers in poly-Si and α-Si phases.

It is known that the binding energy of hydrogen can be substantially perturbed in strained grain-boundary regions. As an example, the binding energy in strained Si-H-Si configuration linearly varies with stretching of Si-Si bond-length in a rate of 0.46eV per 0.1A [11]. This value is taken to estimate UST effect on hydrogen binding. Under the ultrasound, a dynamic stress field generates regions of local expansions and tensions. Amplitude of the average acoustic strain in our UST study is small, of the order of 10^{-3}, and corresponds to bond stretching of 2.5 x 10^{-3}. However, it is anticipated that elastic constants of grain boundaries aresmallerthan that at inter-grain regions. In this case, UST stress will generate a strong local strains at grain boundaries. To quantify the effect, we consider the ratio of grain-boundary volume to inter-grain volume as 1% for 100nm grain size. The amplitude of acoustic strain in grain boundary will approach 10^{-1} corresponding to 10% stretching of bond-length by 0.25. As a result, the reduction of hydrogen binding energy by about 1eV is expected. This rough estimation requires a comprehensive theoretical analysis.

References.
1. W.B.Jackson, N.M.Johnson, C.C.Tsai, I.-W. Wu, A.Chiang, and D.Smith, APL, **61**, 1670 (1992).
2. N.H.Nickel, N.M.Johnson, and C.Van der Walle, Phys.Rev.Lett, **72**, 3393 (1994).
3. S.Ostapenko, L.Jastrzebski, J.Lagowski, and R.K.Smeltzer, APL, **68**, 2873 (1996).
4. S. Ostapenko, N.E. Korsunskaya, M.K.Sheinkman, and S.Koveshnikov, "Defect engineering in semiconductors using ultrasound treatment" in *Encyclopedia of Electrical and Electronics Engineering*, (editor J.G.Webster), in press.
5. Y.Koshka, S.Ostapenko, T.Ruf, and J.M.Zhang, APL, **69**, 2537 (1996).
6. http://www.eng.usf.edu/CMR/smd
7. A.U.Savchouk, S.Ostapenko, G.Nowak, J.Lagowski and L.Jastrzebski. APL, **67**, 82 (1995).
8. M.Tajima, J.Cryst.Growth, **103**, 1 (1990).
9. R.A.Street, Advances in Physics, **30**, 593 (1981).
10. N.H.Nickel, N.M.Johnson, and W.B.Jackson, APL, **62**, 3285 (1993).
11. C.G.Van de Walle and N.H.Nickel, Phys.Rev.B, **51**, 2636 (1995).

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