Enhanced hydrogenation in polycrystalline silicon thin films using low-temperature ultrasound treatment

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

R. K. Smeltzer
David Sarnoff Research Center, Princeton, New Jersey 08543

Ultrasound treatment (UST) was applied to improve electronic properties of polycrystalline silicon films on silica-based substrates. 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. This is accompanied by improvement of a film homogeneity as confirmed by spatially resolved photoluminescence study. The UST effect on sheet resistance demonstrates both stable and metastable behavior. A stable UST effect can be accomplished using consecutive cycles of UST and relaxation. An enhanced passivation of grain boundary defects after UST is directly measured by nanoscale contact potential difference with atomic force microscope. Two specific UST processes based on interaction between the ultrasound and atomic hydrogen are suggested: enhanced passivation of grain boundary defects and UST induced metastability of hydrogen related defects. © *1996 American Institute of Physics.* [S0003-6951(96)03420-1]

Polycrystalline silicon (poly-Si) thin films on glass or fused silica substrates are promising for thin-film transistor (TFT) technology in active matrix liquid crystal displays. Compared with transistors using amorphous silicon films, poly-Si TFTs 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 parameters of poly-Si TFTs.[1,2] The hydrogen defect passivation occurs in two steps: plasma penetration and a subsequent hydrogen diffusion. The diffusion of hydrogen in poly-Si is slow compared with single-crystal silicon due to a trap limiting mechanism at grain boundaries,[3] typically resulting in a long hydrogenation time and electrical inhomogeneity within passivated regions of poly-Si.

In this letter we present a new approach to enhance hydrogenation efficiency in poly-Si thin films using the ultrasound treatment (UST). Defect engineering using the method of UST was proven to be extremely beneficial in polycrystalline silicon where ultrasound vibrations enhance an interaction between extended lattice defects, like grain boundaries and dislocations, with mobile point defects.[4] We report here that the atomic hydrogen is a specifically suitable object for ultrasound stimulated processes in poly-Si thin films.

Semi-insulating silicon films with thicknesses ranging from 0.35 to 0.55 μm were deposited at 625 or 550 °C on Corning 7059 glass or fused silica substrates by low pressure chemical vapor deposition. The 625 °C films had a crystalline structure. The films deposited at 550 °C were amorphous, and their annealing under nitrogen flow for 8–75 h at 550 °C caused a gradual crystallization. The poly-Si films were selectively plasma hydrogenated using a pattern defined by an opening in an Al mask. This enabled us to study the UST effects by comparing hydrogenated with nonhydrogenated areas on the same film. The hydrogenation was performed at 300 °C in a parallel plate rf plasma system operating at a 100 cm H_2 flow with 0.3 Torr pressure and 200 W radio frequency power or using a low pressure electron cyclotron resonance (ECR) plasma system. For UST experiments, ultrasound vibrations were applied to poly-Si films through a glass or fused silica substrates from external circular piezoceramic transducers of 37 or 70 mm diam and 3 mm thickness. Transducers were driven by a function generator and power amplifier adjusted to the resonance frequency of the transducer radial or thickness vibrations. Each UST is specified by a set of parameters: ultrasound mode and frequency (25–650 kHz); amplitude of acoustic strain generated by transducer, typically, on the order of 10^{-5}; temperature from 20 to 100 °C; and UST time of 5–120 min. The temperature of a sample during UST was measured *in situ* by a remote infrared pyrometer, while the amplitude of the acoustic vibrations was controlled by a miniature piezoelectric detector.

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 nanoscale contact potential difference (CPD) mapping were performed. The CPD mapping with spatial resolution of 20 nm was performed in a two-step procedure using the atomic force microscope ''Nanoscope III.'' In the first step, a regular topographic map of a poly-Si surface was obtained by a standard AFM scan in the ''tapping'' mode. In the second step, the AFM tip was lifted over a sample surface with an elevation of 20 nm. This constant elevation was accurately maintained by a computer control system during the second map, and therefore, the tip-to-sample capacitance was maintained constant. When an external ac voltage is applied to the AFM tip, the amplitude of the
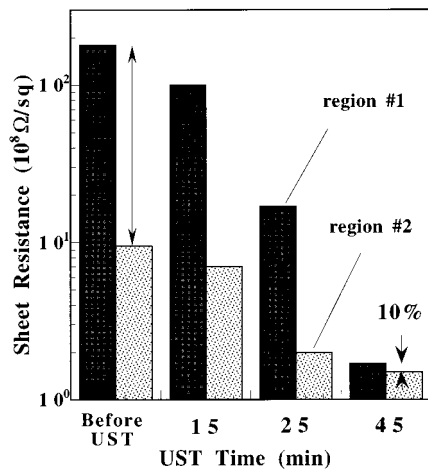
[a]Electronic mail: ostapenk@cmd.usf.edu

FIG. 1. Effect of ultrasound treatment on the reduction of sheet resistance in two different regions (No. 1 and No. 2) of a hydrogenated polysilicon thin film. UST parameters: acoustic strain 10^{-5}, frequency 70 kHz, temperature 55 °C. Initial resistance of nonhydrogenated film was $(5-8) \times 10^{10}$ Ω/sq.

FIG. 2. UST change in a distribution of room-temperature PL intensity ($h\nu_{PL} = 0.75$ eV) on hydrogenated poly-Si film. In inset: increase of PL intensity vs ECR plasma hydrogenation time.

first harmonic of tip oscillations is proportional to the tip-to-sample potential difference. Using a compensating dc voltage, we obtained the spatial distribution of contact potential difference in the poly-Si surface in a form of CPD map. Details of the CPS technique have been published elsewhere.[5]

We have found that plasma hydrogenation applied to poly-Si films reduces resistance by a factor of one order of magnitude which is consistent with previously published plasma hydrogenation data.[6] We notice that the decreased resistance is saturated to a minimum value of the order of 10^9 $\Omega/\square$ after 3–5 h rf plasma processing of 0.35 μm 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 the UST (Fig. 1). Resistance in nonhydrogenated region was practically not changed after the UST. Our control 100 °C annealing of the same hydrogenated films without UST did not reveal a change in resistance with accuracy of 10%. We notice that the UST-induced reduction of sheet resistance occurs at temperatures lower than 100 °C, which is specifically beneficial for large scale poly-Si TFT applications requiring low-cost glass substrates with low thermal stability. By varying the UST time, we found that the kinetics of the UST effect is characterized by a time constant of 25 min at 55 °C. Another feature of the UST effect is an improvement of resistance homogeneity within the same poly-Si film. In Fig. 1 we present the UST induced change of resistance in two regions (No. 1 and No. 2) of the same film. Initially, a more than one order of magnitude variation in resistance was reduced to ~10% after a few consecutive steps of UST. Based on these findings, we may suggest 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 and nanoscale CPD study.

At 4.2 K the 0.9 eV PL band corresponding to band-tail recombination dominates in the luminescence spectrum of films deposited at 625 °C. With increasing temperature, the
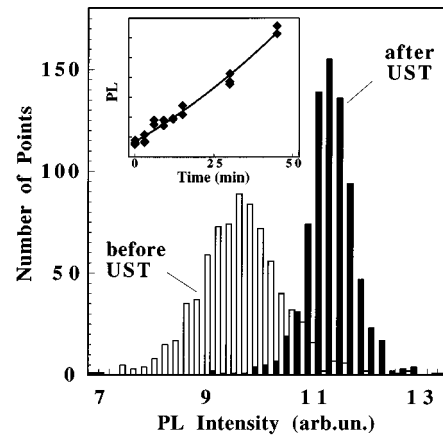
0.9 eV band is strongly quenched and an oxygen-related PL bands with maxima at 0.65 and 0.72 eV are retained and persist at room temperature.[8,9] We used these ''oxygen'' PL bands intensity to monitor the result of hydrogenation and UST on poly-Si film properties. In Fig. 2 (inset), the increase of the 0.72 eV PL band intensity versus ECR plasma hydrogenation time is shown. This increase of PL intensity occurs due to hydrogen passivation of nonradiative recombination centers at grain boundaries.[7] We used the PL mapping technique with a resolution of 100 μm to monitor the distribution of recombination centers and changes after UST. The results are presented in Fig. 2 as two histograms of exactly the same hydrogenated film area prior to and immediately after UST. 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 in the mapped region. This result is consistent with the UST-induced improvement of resistance homogeneity shown in Fig. 1.

Contact potential difference (CPD) mapping using the atomic force microscope with a resolution of 20 nm is presented in Fig. 3(a) for the film subjected to 30 min ECR hydrogenation. CPD contrast originates from the charge trapped at grain boundary defects in poly-Si. The contrast of a CPD map is gradually reduced with hydrogenation time due to passivation of grain boundary defects.[10] We performed the UST on hydrogenated films and compared CPD contrast before and after treatment [Figs. 3(a) and 3(b)]. We precisely maintained the measurement condition of CPD mapping in both cases, in particular, the elevation of a tip above sample surface. The reduction of the CPD contrast after UST is seen and quantified by a narrowing of the contact potential histogram in Figs. 3(c) and 3(d). The UST effect on CPD mapping contrast provides a direct proof of ultrasound enhanced hydrogenation of grain boundary defects in poly-Si

The stability of the UST effect on sheet resistance was examined. We found that the UST-induced reduction of sheet resistance in a hydrogenated region partially recovers after storage in the dark at room temperature for 10–12 h (see Table I).1 We noticed, however, that the value of resistance after relaxation was not exactly the same as the initial
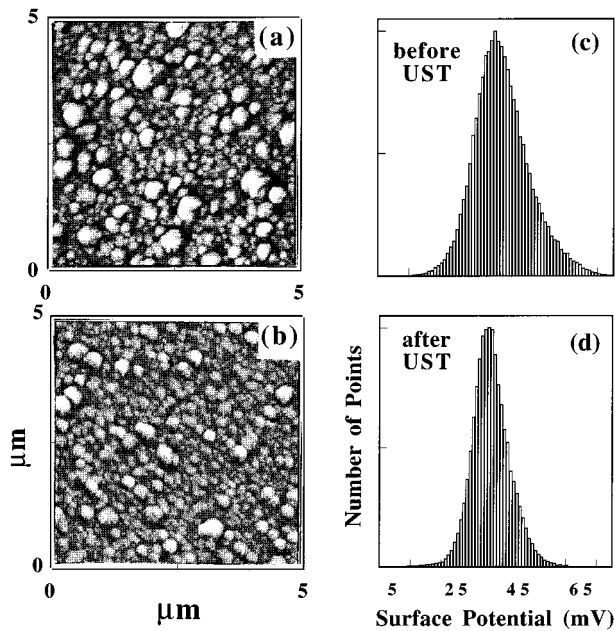
FIG. 3. Contact potential difference mapping (5×5 μm) of poly-Si films before (a) and after UST (b). The (c) and (d) are histograms of contact potential distribution across mapped areas shown in (a) and (b), respectively.

one, but usually lower. Using consecutive cycles of UST and relaxation, we were able to stabilize a reduced sheet resistance on the level about one order of magnitude lower compared with the initial value (Table I). This final value of resistance did not show any significant change for one month at room temperature. This relaxation study suggests that two competing UST processes occur in hydrogenated films. One of them produces a stable reduction of sheet resistance, while the second promotes a metastable phenomenon. We notice that the change of CPD contrast presented in Fig. 3 corresponds to the stable UST effect. Based on our findings, we suggest that these two parallel processes are attributed to: (a) stable passivation with atomic hydrogen of grain boundary defects (e.g., dangling bonds), which is responsible for a permanent change of sheet resistance and CPD contrast, and (b) UST generation of metastable hydrogen-related defects responsible for relaxation behavior.

It is known that after plasma hydrogenation the total hydrogen concentration in poly-Si films can exceed the number of nonpassivated dangling bonds by as much as two orders of magnitude.[11] Therefore, a significant reservoir of

TABLE I. Cyclic UST and relaxation at hydrogenated poly-Si thin films. (UST was performed at 60 °C for 30 min, relaxation at 20 °C for 12 h.)

Film processing	Cycle no.	Film resistance normalized to initial value
Initial	⋯	1.0
UST	1	.21
Relaxation		.70
UST	2	.07
Relaxation		.12
UST	3	.02
Relaxation		.11

electrically nonactive hydrogen is available in poly-Si films after hydrogenation. It had been observed that the hydrogen in this reservoir is weakly bound and can be released using a low-temperature annealing at 460 K followed by a rapid quenching.[6] A thermal liberation of hydrogen from the reservoir requires an activation energy of about 1 eV. After fast diffusion to grain boundary regions, this atomic hydrogen can be captured by dangling bonds and form stable at room temperature centers or, alternatively, form electrically active metastable hydrogen-related complexes. The Si–Si bonds at grain boundaries are metastable donors responsible for the relaxation of resistivity change after annealing and quenching of poly-Si films.[6,12]

We postulate that low-temperature UST can promote a hydrogen liberation from the reservoir, presumably as a result of decreasing the binding energy of the atomic hydrogen in reservoir. Due to a competition of the stable (a) and the metastable (b) processes, cyclic UST and relaxation are necessary to bring together released hydrogen and dangling bonds at grain boundaries, which results in formation of stable Si–H centers.

It is recognized that extended defects such as grain boundaries and dislocations can effectively absorb the ultrasound and transfer its energy to mobile point defects. In this respect, the atomic hydrogen introduced by plasma treatment into polycrystalline silicon is a favorable application for UST processing. The reported effects of stable UST passivation of grain boundary defects may be a cause of UST improvement of the leakage current recently observed in hydrogenated poly-Si TFTs.[13]

[1] I. W. Wu, T. Y. Huang, W. B. Jackson, A. G. Lewis, and A. Chiang, IEEE Electron Device Lett. **12**, 181 (1991).
[2] R. A. Ditizio, G. Liu, S. J. Fonash, B. C. Hseih, and D. W. Greve, Appl. Phys. Lett. **56**, 1140 (1990).
[3] W. B. Jackson, N. M. Johnson, C. C. Tsai, I.-W. Wu, A. Chiang, and D. Smith, Appl. Phys. Lett. **61**, 1670 (1992).
[4] S. Ostapenko, J. Lagowski, L. Jastrzebski, and B. Sopori, Appl. Phys. Lett. **65**, 1555 (1994).
[5] H. Yokoyama and T. Inoue, Thin Solid Films **242**, 33 (1994).
[6] N. H. Nickel, N. M. Johnson, and C. Van der Walle, Phys. Rev. Lett. **72**, 3393 (1994).
[7] A. U. Savchouk, S. Ostapenko, G. Nowak, J. Lagowski, and L. Jastrzebski, Appl. Phys. Lett. **67**, 82 (1995).
[8] M. Tajima, J. Cryst. Growth **103**, 1 (1990).
[9] O. King and D. G. Hall, Phys. Rev. B **50**, 10661 (1994).
[10] G. Nowak and J. Lagowski (unpublished).
[11] N. H. Nickel, N. M. Johnson, and W. B. Jackson, Appl. Phys. Lett. **62**, 3285 (1993).
[12] C. Van der Walle and N. H. Nickel, Phys. Rev. B **51**, 2636 (1995).
[13] S. Ostapenko, W. Henley, S. Karimpannakkel, L. Jastrzebski, and J. Lagowski, *Defects and Impurity Engineered Semiconductors and Devices*, edited by S. Ashok, J. Chevallier, I. Akasaki, N. M. Johnson, and B. L. Sopori (MRS Proceedins, Pittsburgh, PA, 1995), Vol. 378, p. 405.