<table>
<thead>
<tr>
<th>Title</th>
<th>Role of Hydrogen in Polycrystalline Si by Excimer Laser Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>KAWAMOTO, Naoya; MATSUO, Naoto; MASUDA, Atsushi; KITAMON, Yoshitaka; MATSUMURA, Hideki; HARADA, Yasunori; MIYOSHI, Tadaki; HAMADA, Hiroki</td>
</tr>
<tr>
<td>Citation</td>
<td>IEICE TRANSACTIONS on Electronics, E88-C(2): 241-246</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2005-02-01</td>
</tr>
<tr>
<td>Type</td>
<td>Journal Article</td>
</tr>
<tr>
<td>Text version</td>
<td>publisher</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10119/4728">http://hdl.handle.net/10119/4728</a></td>
</tr>
</tbody>
</table>
Role of Hydrogen in Polycrystalline Si by Excimer Laser Annealing

Naoya KAWAMOTO††††, Nonmember, Naoto MATSUO††, Atsushi MASUDA†††, Members, Yoshitaka KITAMON†, Hideki MATSUMURA†††, Yasunori HARADA††, Tadaki MIYOSHI†, Nonmembers, and Hiroki HAMADA††††, Member

SUMMARY The role of hydrogen in the Si film during excimer laser annealing (ELA) has been successfully studied by using a novel sample structure, which is stacked by a-Si film and SiN film. Hydrogen contents in the Si films during ELA are changed by preparing samples with hydrogen content of 2.3–8.2 at.% in the SiN films with a use of catalytic (Cat)-CVD method. For the low concentration of hydrogens in the Si film, the grain size increases by decreasing hydrogen concentration in the Si film, and the internal stress of the film decreases as increasing the shot number. For the high concentration of hydrogens in the Si film, hydrogen burst was observed at 500 mJ/cm² and the dependence of the internal stress on the shot number becomes weak even at 318 mJ/cm². These phenomena can be understood basically using the secondary grain growth mechanism, which we have proposed.

key words: polycrystalline Si, excimer laser annealing, hydrogen, secondary grain growth, stress relaxation, Cat-CVD

1. Introduction

Polycrystalline Si (poly-Si) film recrystallized by excimer laser annealing (ELA) has been studied intensively focusing both on the nucleation and crystal growth mechanisms because it is attractive for application to thin film transistors (TFTs) [1]–[4].

We have studied the crystal growth mechanism of the poly-Si film prepared by ELA [5]–[12]. The electron spin resonance (ESR) measurement for ELA poly-Si film indicated that the density of the defects at the grain boundary such as the dangling bonds is much larger than that of the in-grain defects [5]. The hydrogen in the amorphous Si (a-Si) film strongly affects the spin density even after the recrystallization of the poly-Si film by ELA [6]. To clarify the hydrogen role further, we investigated the characteristics of the recrystallized poly-Si film on SiO₂/SiN/glass. Here, the SiN films are deposited by plasma-enhanced chemical vapor deposition (PECVD), and the hydrogen concentration of a SiN film is large. Then, we inferred the nucleation model related to the hydrogen supplied from the SiO₂/SiN/glass [10]–[12]. It was found that hydrogen supply from the substrate was the dominant factor to determine the morphology and grain size of poly-Si.

Considering our experimental results, it is thought that the difference in grain size of the poly-Si film between on a SiN film and on a glass substrate is attributed to hydrogen in the SiN film and the thermal conductivity of the substrate. Therefore, a quantitative supply of the hydrogens to the melt-Si from the SiN film is necessary to understand what role the hydrogens have during the crystallization by ELA.

In this study, we clarify the influence of hydrogen concentration in the Si film on morphology, defect density and internal stress of poly-Si experimentally, and verify the crystallization model [8] which were presented by our group. The hydrogens are introduced in the melt-Si film from the catalytic chemical vapor deposition (Cat-CVD) SiN films including hydrogens of 2.3, 4.2 and 8.2 at.\%.

2. Experimental

An a-Si film was deposited on the SiN/quartz substrate by low-pressure chemical vapor deposition (LPCVD) method using Si₂H₆ at 450°C. The thickness of a-Si film was 50 nm. SiN film was deposited by Cat-CVD method [13]. The following deposition conditions were employed. The flow rates of SiH₄ and NH₃ were 2 and 200 sccm. The pressure in the deposition chamber was 4 Pa. The catalyst temperature was kept at 1650°C. The hydrogen concentration of SiN film was controlled by changing the substrate temperature during the deposition: The hydrogen concentrations of 2.3, 4.2 and 8.2 at.% correspond to substrate temperature of 400, 300 and 200°C, respectively. The hydrogen concentration is given by measuring the signal intensity of Si-N stretching mode (FTIR). The refractive index of SiN film for 2.3 and 4.2 at.% hydrogen was 2.0 and that for 8.2 at.% was 1.95. The thickness of SiN film was 42 nm. The KrF multi-pulse excimer laser was irradiated to the a-Si film at 1 Hz and at room temperature under approximately 10⁻⁴ Pa. The irradiation time was 23 ns at full width at half maximum (FWHM). The energy density and shot number were 318 to 500 mJ/cm² and 8 to 300 shots, respectively. The hydrogens are introduced into the melt-Si from the SiN film during the ELA [12]. The concentration of hydrogens in the poly-Si film are...
close and proportional to that in the SiN film, although they are not measured precisely. The crystallinity and surface morphology of the poly-Si film were measured by Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron spin resonance (ESR). Raman spectroscopy was carried out with backscattering geometry and a 514.5 nm Ar ion laser with a spot size of 0.8 \( \mu \)m. The FWHM of the transverse optical (TO) Raman peak of Si(100) wafer was 4.2 cm\(^{-1}\). Secco etching was performed before observing the poly-Si surface by SEM to clarify the film structure and the morphology. The temperature of ESR measurement, the center and range of the magnetic field and power were 10 K, 3367 G, 100 G and 40 \( \mu \)W, respectively.

3. Results and Discussion

3.1 Influence of Hydrogen Concentration on Morphology, Defect Density and Internal Stress of Poly-Si Film

Figure 1 shows the relationship between the FWHM of the Raman peak and the energy density at 8 shots. The FWHM values are nearly constant for the energy density of 318 to 500 mJ/cm\(^2\) and hydrogen concentration of 2.3 and 4.2 at.%. FWHM of Raman peak is related to the defects in the Si [14]. The crystal defect density is nearly constant at 2.3 and 4.2 at.% of hydrogens. The reason why it drastically increases at 500 mJ/cm\(^2\) and hydrogen concentration of 8.2 at.% is due to the hydrogen burst, which we have examined by cross section TEM. It is found that the hydrogen behavior introduced in the melt-Si is very sensitive to the hydrogen concentration and the energy density.

Figure 2 shows the cross section TEM image of the poly-Si at 500 mJ/cm\(^2\) and 8 shots for hydrogen concentration of 2.3 at.% and 8.2 at.%. The poly-Si film is formed uniformly. It is indicated that the poly-Si is formed uniformly at the ELA conditions of present experiment except for 500 mJ/cm\(^2\) and 8.2 at.%.

Figure 3 shows the relationship between \( \Delta \omega \) and shot number. This experiment was conducted at 318 mJ/cm\(^2\) to eliminate the hydrogen burst during the ELA. \( \Delta \omega \) is the difference of the Raman peaks between the c-Si (521 cm\(^{-1}\)) and poly-Si. \( \Delta \omega \) corresponds to the tensile stress \( \tau \) in the poly-Si grains as shown by eq.(1) [14].

\[
\tau [\text{dyn/cm}^2] = 2.49 \times 10^9 \times \Delta \omega [\text{cm}^{-1}]
\]  

Although \( \Delta \omega \) decreases drastically with increasing the shot number for 2.3 and 4.2 at.%, it decreases gently with the shot number for 8.2 at.%. This result shows that the stress relaxation of poly-Si with hydrogen concentration of 8.2 at.% in SiN film is smaller than that of 2.3 and 4.2 at.%. The phenomenon that the stress relaxation proceeds with increasing the shot number for 2.3 and 4.2 at.% also indicates that the secondary grain growth proceeds with the shot number.

Figures 4(a) and (b) show the SEM images of 2.3 and 4.2 at.% for 318 mJ/cm\(^2\) and 8 shots, respectively. The grain size of poly-Si with 2.3 and 4.2 at.% are estimated to be 575 and 252 nm, respectively. The grain size of 2.3 at.% is larger than that of 4.2 at.%. It is found that the secondary grain growth activates the stress relaxation.

Figure 5 shows the ESR result at 500 mJ/cm\(^2\) for 2.3 at.%. The signal of \( g = 2.0055 \) and that of \( g = 2.0007 \) correspond to the dangling bond in the poly-Si film and that in the quartz substrate, respectively. The spin density in the poly-Si film for hydrogen concentration of 2.3 at.% in SiN film is \( 2.1 \times 10^{19} / \text{cm}^3 \). It is thought that the origin of the spin density is the crystal defects at the grain boundary, as we already pointed at [5].

3.2 Crystallization Model

The results shown in the previous section are clearly un-
understood by using following the model. Figure 6 shows the model of the secondary grain growth under the solid phase crystallization (SPC). We already reported that the grain enlargement of poly-Si under the solid phase occurs by carrying out the multi-pulse laser irradiation at low energy density [3]. The theory of the secondary grain growth by the SPC was studied by Thompson [15], and our proposed model also assumes the SPC process [4],[5]. The present model was constructed by taking into considerations of the following experimental results. First, in-grain defects disappear under the laser irradiation because of the defects movement to the grain boundary [5]. Second, the rapid secondary grain growth occurs when the laser energy density and shot number reach critical values [6]. These phenomena indicate that the secondary grain growth occurs when the sum of the laser energy density and the crystal defects energy per unit area becomes a critical value. Si atoms in the grain with nonpreferred orientation move to the grain with preferred orientation via the grain boundary. The grain boundary movement from the left to right occurs. The secondary grain growth and the internal-stress relaxation, which proceed through the secondary grain growth, occur simultaneously. The present model assumes that the strain energy, which is generated by the crystal defect at the grain boundary, is released at the start of the secondary grain growth. The hydrogen atoms incorporated in the Si during the ELA form the hydrogen-vacancy pair at the grain boundary and it prevents the secondary grain growth. Therefore, the grain size increases with decreasing the hydrogen concentration. Our experimental results support the present growth model as follows. First, the internal stress of the poly-Si film decreases as increasing the shot number as explained in Fig. 3. The grain enlargement is observed as increasing the shot number. This phenomenon fits to the model in the point that the secondary grain growth leads to the internal-stress relaxation. Second, the grain size of poly-Si secondary grain with 2.3 at.% is larger than that with 4.2 at.% as shown in Fig. 4. This phenomenon also fits to the present model from a viewpoint of the effect of hydrogen on the grain growth. It was also reported that the grain sizes of poly-Si with hydrogen concentrations of 1.3 and 2.8 at.% are 500 and 150 nm, respectively [16]. It seems to be right that the hydrogen concentration in the Si film influences the grain size.

The present model does not apply to high concentration of hydrogen, such as 8.2 at.%. The stress relaxation...
also has a close relationship with the hydrogen concentration. Thus, it is important for the secondary grain growth utilizing ELA to decrease the hydrogen concentration in the Si film. The formation of SiN film on the glass substrate is also necessary from a viewpoint of suppressing the diffusion of contaminations such as K or Na into the a-Si layer. The advantage of Cat-CVD method comparing with thermal CVD and PECVD method to prepare SiN film with low hydrogen concentration was shown in ref 13. The formation of SiN film with low H concentration by Cat-CVD process is necessary to realize high reliability of the TFTs.

4. Conclusions

The influence of hydrogens, which was introduced from the Cat-CVD SiN film into the melt-Si film, on the laser crystallization of Si was examined. For the poly-Si film with a low hydrogen concentration crystallized on the SiN film from 2.3 to 4.2 at.% hydrogens, the stress relaxation of poly-Si proceeded with increasing the shot number and the grain size increased as decreasing the hydrogen concentration. The defect density at the grain boundary deduced from the spin density was $2.1 \times 10^{19} \text{cm}^3$. For the poly-Si film with a high hydrogen concentration crystallized on the SiN film of 8.2 at.% hydrogens, the hydrogen burst occurred at 500 mJ/cm² and the dependence of the internal stress of the poly-Si film on the shot number becomes weak even at 318 mJ/cm². These results dependent on hydrogen concentration support the crystallization model which we have already proposed. The present model is effective to clarify precisely the laser crystallization phenomenon of the Si film including hydrogens with low concentration. And also Si/SiN film structure is very useful to obtain large grain sized poly-Si films using Si/SiN film structure.

References

Naoto Matsuo received the B.S. and M.S. degrees in metal science and technology and Dr. Eng. degree in electrical engineering, all from Kyoto University, Kyoto, Japan, in 1978, 1980 and 1993, respectively. From 1980 to 1992, he was engaged in the research and development for the process, materials and devices of ultra-large scale integrated circuit (ULSI) at the Matsushita Electric Industrial Co. Ltd. From 1993 to 1994, he was a research student at Kyoto University, where he studied the solid-state physics and devices for the future electronics, and also a part time Assistant Professor at Yamaguchi University. In 1994 he joined the Department of Electrical and Electronic Engineering, Yamaguchi University, as an Associate Professor, where his research topic was electric conduction mechanism of very thin SiO₂ film, nanometer-size MOS device utilizing the tunnel-effect and crystallization of a-Si on glass by excimer laser annealing. Currently he is a Professor of Graduate School of Engineering, University of Hyogo. His interest focuses on the functional materials and new devices including ULSI and Flat Panel Display. He is an author or coauthor of more than 130 technical papers including more than 80 academic journal papers, and also patent holder of 12 Japan and U.S. patents. He also published 1 textbook “Semiconductor Devices—Based on Operation Principles” (ISBN4-339-00726-9). He was a Program Co-Chair of 2001–2002 Asia-Pacific Workshop on Fundamental and Application of Advanced Semiconductor Devices (AWAD) and a Workshop Chair of AMD (Active-Matrix Display) in 2003 International Display Workshops(IDW’03), and will serve as a Program Chair of 2005 International Workshop of Active-Matrix LCD(AM-LCD’05). He is an editor of the IEICE Transactions of Electronics from 2003. Dr. Matsuo is a member of The Japan Society of Applied Physics, The Japan Institute of Metals and IEEE Electron Device Society.

Atsushi Masuda received his M.E. and Ph.D. degrees in Engineering both from Kanazawa University, Japan in 1992 and 1996, respectively. In 1992 he joined Materials Research Laboratory, Fuji Xerox Co., Ltd. and in 1996 he joined Japan Advanced Institute of Science and Technology (JAIST). His main research field is preparation and characterization of thin-film electronic materials, for example, amorphous semiconductors and inorganic materials, especially by catalytic chemical vapor deposition. He is currently a research associate of School of Materials Science of JAIST. He is a steering committee member of AMLCD ’03-’05 and an organizing committee member of EM-NANO 2004. He is an author and co-author of over 150 technical papers and conference papers, and an author of two books chapter on thin-films. He has applied for over 30 foreign and domestic patents. He is a senior member of the Japan Society of Applied Physics, the Ceramic Society of Japan and the Vacuum Society of Japan.

Hideki Matsumura received his B.S. degree in electronic engineering for the study of liquid crystals from the University of Electro-Communications at 1970, M.E. and Ph.D. degrees for the study of ion-implantation from Tokyo Institute of Technology at 1972 and 1975, respectively. In 1975, he joined University of Surrey, England, as a Research Fellow of Electronic and Electrical Engineering Department and continued the work of ion-implantation. In 1977, he joined Tokyo Institute of Technology as a Research Associate and started the study on amorphous silicon. In 1983, he joined Hiroshima University as an Associate Professor, continued the work of amorphous materials and in 1985 he developed a low temperature thin film technology called Cat-CVD. In 1992, he joined a newly established Institute, JAIST (Japan Advanced Institute of Science and Technology), as a Professor of School of Materials Science, and continued the work of Cat-CVD technology for various applications. From 1998 to 2001, he was a leader of a national project, Application of Cat-CVD Technology on Semiconductor Devices. He was one of starting members and also the 1st general chairman of the 1st International Conference of Cat-CVD (Hot-Wire CVD) Process, held at Kanazawa in 2000. He has been also one of committee members of several meetings concerned with Cat-CVD technology, solar cell technology and display technology.

Yasunori Harada received Dr.Eng. degree from the Graduate School of Engineering, Hiroshima University, Hiroshima, Japan, in 1990. He studied the Materials Science and Metallic Materials. He was a research associate at Hiroshima University in 1989. From 1990 to 2003, he worked at the Department of Production Systems Engineering, Toyohashi University of Technology, Aichi. He investigated the Metal Forming Processes, Mechanics of Deformation, Joining Process and Surface Modification. In 2003, he joined the Graduate school of Engineering at University of Hyogo. Presently, he is an Associate Professor. His research area is the Metal Forming Processes and Surface Modification. He is a member of the Japan Institute of Metals, the Iron and Steel Institute of Japan, the Japan Society for Technology of Plasticity, the Japan Society of Mechanical Engineers and Japan Society of Shot Peening Technology.

Tadaki Miyoshi graduated from Osaka University in 1969. He received the M.E. and D.Eng. degrees from Osaka University in 1971 and 1976, respectively. From 1976 to 1978 he was on the faculty of Yamaguchi University as a lecturer, from 1979 to 1988 as an associate professor, and from 1988 to 1990 as a professor. He has been a professor on the Faculty of Engineering, Yamaguchi University, since October 1990. He has investigated the optical properties of semiconductor nanocrystals. He is a member of The Physical Society of Japan, The Physical Society of Applied Physics, and The Institute of Electrical Engineers of Japan.
Hiroki Hamada received his B.S., M.E. and Ph.D. degrees in electronic engineering from Kinki University, Japan in 1975, 1977, and 1980, respectively. In 1980 he joined SANYO Electric Co. Ltd., Osaka, where he engaged in the research and development of semiconductor laser for Compact Disk (CD) and Digital Video Disk (DVD). In 1992–2002, he engaged in the research and development of low & high-temperature processed poly-Si TFT LCDs and Active-Matrix OLEDs. Since 2002, he has been working on the development of inorganic EL displays. He is currently a senior manager of Material and Devices Development Center Business Unit. He received the paper award in 2003 from the IEICE for development of HD-LCD light-valves using poly-Si TFTs. He served as a program committee of AMLCD’96–’01, and as a program chair of AMLCD’02, and as a program committee of workshop on Active-Matrix Display in IDW’97–’99 and IDW’02–’03, and as a chair of workshop on Active-Matrix Display in IDW’00–’01, and serve as a stealing chair of AMLCD’04, and as a program committee of workshop on Active-Matrix Display in IDW’04 and as an editor of the IEICE. He is an author and co-author of over 100 technical papers and conference papers, and an author of two books chapter on low-temperature processed poly-Si TFT LCDs. He has applied for over 100 foreign and domestic patents. He is a senior member of the IEEE LEOS & ED, a member of the Society for Information Display, the Japan Society of Applied Physics, and the Laser Society of Japan.