Extended Abstracts of the 18th (1986 International) Conference on Solid State Devices and Materials, Tokyo, 1986, pp. 217-220

Photochemical Vapor Deposition of Single-Crystal Silicon at a Very Low Temperature of 200 °C

A.Yamada, S.Nishida, M.Konagai, and K.Takahashi

Department of Physical Electronics, Tokyo Institute of Technology

2-12-1, O-okayama, Meguro-ku, Tokyo 152, JAPAN

A novel Si epitaxial growth technique has been developed using mercury-sensitized photochemical vapor deposition. Epitaxial thin layers were grown on (100) Si substrates at 100-300°C from gas mixture of $Si_2H_6+SiH_2F_2+H_2$ or $SiH_4+SiH_2F_2+H_2$ by irradiation of a low pressure mercury lamp(1849Å, 2537Å). Reflective high-energy electron diffraction and Raman scattering spectroscopy showed that the epitaxial layers had good crystallinities. The epitaxial layers were characterized by the van der Pauw Hall mesurements and secondary ion mass spectroscopy.

§1. Introduction

The development of low-temperature processes for fabricating integrated circuits has become essential for an achievement of higher operating speeds and for an increase of circuit densities. In particular, a low-temperature process for depositing epitaxial silicon will be necessary for realization of future devices. Several methods have been proposed for this purpose, such as molecular beam epitaxy[1)], low pressure chemical vapor deposition[2)] and plasma enhanced chemical vapor deposition (PECVD)[3)]. These techniques have an advantage in using low substrate temperatures of about 600°C. However, they have limitations due to the low productivity and/or the difficulty to control the reactive species.

Recently, photoepitaxy has an attractive interest in a new method for lowering the growth temperature[4),5),6)] because the reactant gases are not decomposed thermally but photochemically. In addition, the light irradiation may be effective in the enhancement of the surface reaction and in the migration of film precusors on the substrate surface. Furthermore, the photo-CVD technique possesses the advantage of reaction selectivity; only necessitated molecules or radicals could be excited.

In this work, a drastic reduction of the growth temperature was realized using the photochemical vapor deposition (photo-CVD) method from $Si_2H_6+SiH_2F_2+H_2$ or $SiH_4+SiH_2F_2+H_2$ gas mixtures. Epitaxial layers were characterized by the reflective high energy electron diffraction (RHEED), the Raman scattering, the secondary ion mass spectroscopy (SIMS), and the van der Pauw Hall measurements.

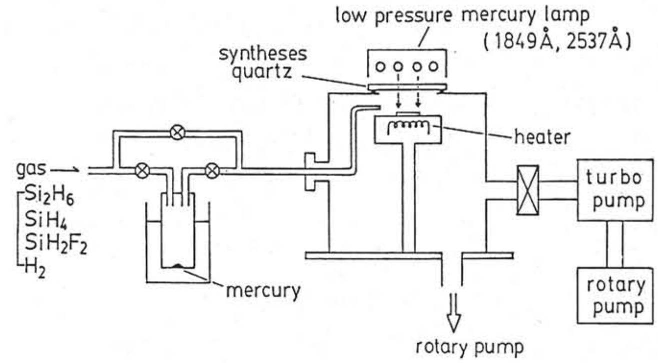

Fig.1 A schematic diagram of our apparatus.

§2. Experimental

Figure 1 shows a schematic diagram of the photo-CVD system. As an ultraviolet light source, a low pressure mercury lamp with a 1849Å and 2537Å resonance lines was used. The lamp was placed on a Suprasil quarz window which covers the top of the reactant chamber. The internal surface of the window was painted with low pressure fluorinated oil to retard the film deposition onto the window itself. A reactant gas was Si_2H_6 (disilane) or SiH_4 (monosilane), introducing into a reactor with SiH_2F_2 (difluorosilane) and H_2 gases. For an enhancement of the gas decomposition, the mercury photosensitization method was employed. Therefore, a very small amount of mercury vapor was carried into the reactor by passing the gases over a mercury reservoir immersed in a water bath at 50°C. Phosphine (PH_3) and diborane (B_2H_6) were used for n-type and p-type doping gases, respectively.

(100)-oriented Si wafers were used as substrates and cleaned in organic solvents, followed by a $HF+NH_4F$ rinse. Special cleaning treatment like a conventional pre-annealing at 800°C was not carried out before epitaxial growth. A turbo molecular pump was connected to evacuate the system below 10^{-6}Torr prior to the growth. During the growth, the gases were exhausted by a rotary pump, and the system was throttled to keep the desired pressure. Typical preparation conditions were summarized in Table I.

§3. Results and discussion

In our previous works, it has been found that the crystallinity of microcrystallized amorphous silicon (μc-Si) deposited on glass substrates by the photo-CVD method was better than that by the plasma chemical vapor deposition method prepared from $Si_2H_6+H_2$ gas mixture[7]. An improvement of the preferential orientation of the films was also observed by addition of SiH_2F_2 gas in the $Si_2H_6+H_2$ system[8]. These results may suggest that low temperature silicon epitaxy could be possible on Si substrates using photo-CVD technique from the $Si_2H_6+SiH_2F_2+H_2$ gas mixture.

Table I. Typical preparation conditions.

$T_{sub.}$ (°C)	Si_2H_6 (sccm)	SiH_4 (sccm)	SiH_2F_2 (sccm)	H_2 (sccm)	Pressure (Torr)
100-300	1		20-30	150	2
250		5	25	50	2

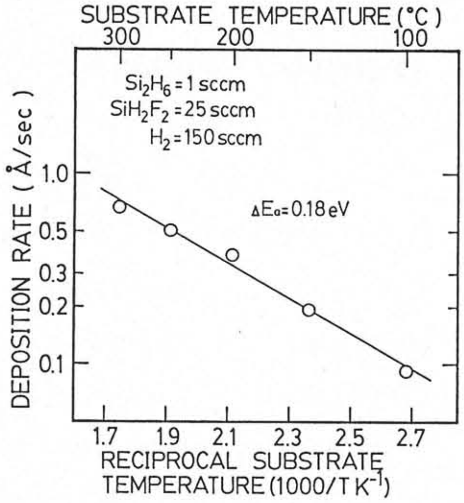

Fig.2 Growth rate as a function of reciprocal temperature.

3.1 Growth rate

Figure 2 shows the growth rate of the layers using Si_2H_6 as a function of the reciprocal substrate temperature. The light intensity was about $30mW/cm^2$ and the increase in the surface temperature due to light irradiation was negligible. In the investigated temperature range of 100-300°C, the epitaxial growth of the layers was confirmed by the RHEED pattern. In Fig.2, it was found that the growth rate was determined by surface reactions, and the activation energy of 4.2kcal/mol was obtained. This value is very small compared with 25kcal/mol of the photoepitaxy using Si_2H_6[6]. From IR measurements, no traces of hydrogen and fluorine atoms in the layers were observed. The crystallinity of the layers was more sensitive to the SiH_2F_2 flow rate than to the substrate temperature.

3.2 RHEED measurements

Figure 3 represents the variation of RHEED patterns of epitaxial layers grown at 200°C correlated to the SiH_2F_2 flow rate using Si_2H_6 as a reactant gas. Without the SiH_2F_2 gas (a), narrow ring pattern which is a typical pattern of microcrystalline material was obtained. With the addition of 15sccm of SiH_2F_2, slight streak lines appeared in the pattern (b). When the SiH_2F_2 flow rate exceeded 20sccm, the layer became epitaxial (c) and the most smooth surface of epitaxial layer was obtained at 35sccm (d). Using SiH_4 as a reactant gas, the RHEED pattern showed

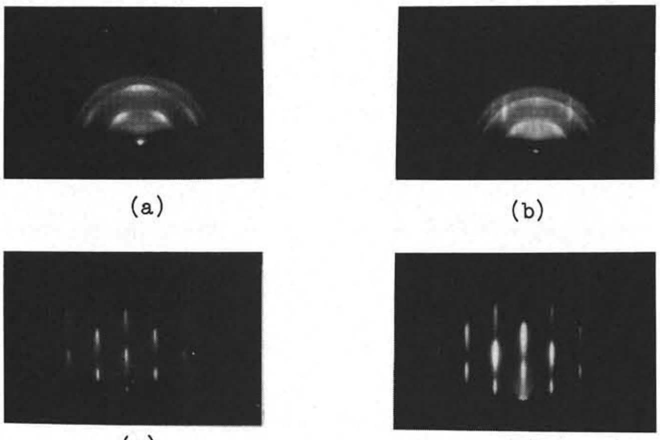

Fig.3 RHEED patterns of films correlated to the SiH_2F_2 flow rate: (a) 0sccm, (b) 15sccm, (c) 25sccm, (d) 35sccm.

elongated streak and clear Kikuchi lines as indicated in Fig.4. From this result, it was found that the layers grown from SiH_4 had good crystallinities and smooth surface morphologies.

The improvement of the crystallinity by addition of SiH_2F_2 gas suggests that fluorine or fluoride radicals may play an important role for the epitaxial growth. First is the removal of the native oxide on Si substrate. Suzuki et al.[9] reported that the crystallinity of plasma-CVD epitaxial layers was improved by introducing a small amount of Ge in an initial stage of the growth, which is considered to be effective to remove the native oxide. In this study, the flourine or fluoride radicals may support the removal of native oxide in a simillar manner as Ge atoms.

Second is the removal of the excess hydrogen from the growing surface. We checked the crystallinity of a layer which was grown from a Si_2H_6+H_2 gas mixture after forming a buffer layer from Si_2H_6+SiH_2F_2+H_2 in the beginning of the

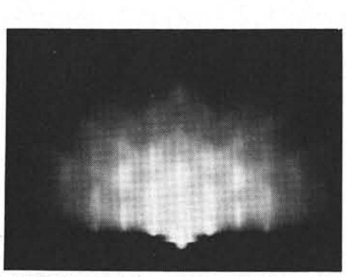

Fig.4 RHEED pattern of photoepitaxial layer using SiH_4 gas.

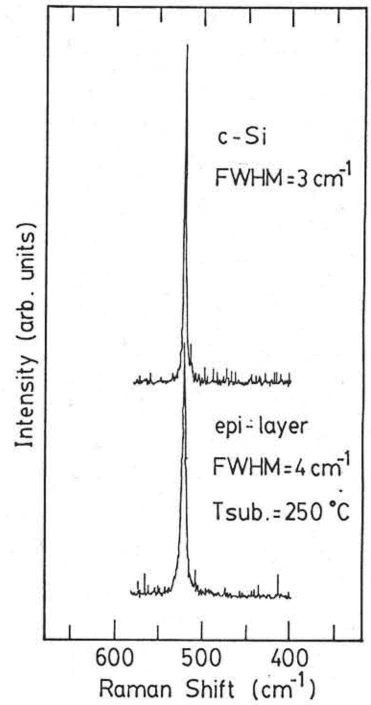

Fig.5 Raman spectra for an epitaxial Si.

growth and found that the grown layer exhibited a poor orientation, just like Fig.3 (b). It was reported that in the mecanism for microcrystallization of a-Si, the hydrogen radicals decrease the barrier height against the surface migration of the precursors by covering the growing surface[10]. However, excess hydrogen radicals cause a considerable fraction of bonded hydrogens at the grain boundaries and these bonded hydrogens behave as steric hindrances against the growth of the crystallite[11]. The presence of SiH_2F_2 in reactant gases is possibly effective for gettering the bonded hydrogen.

3.3 Raman scattering

The Raman scattering measurements were carried out for characterization of the crystallinity of epitaxial layers prepared from Si_2H_6 or SiH_4 gas. The spectrum of the layer grown at 250°C from Si_2H_6 gas exhibited a sharp peak at 520cm^{-1}, identical to that of crystalline Si, and the full width at half maximum (FWHM) of the spectrum was estimated to be about 6cm^{-1}. The FWHM of the spectrum was much improved by using SiH_4 gas. Figure 5 shows the Raman spectra for an epitaxial Si prepared from SiH_4 at 250°C. The spectrum of the epitaxial layer also exhibited a sharp peak at $520cm^{-1}$. The symmetry of the spectrum showed good crystallinity of the epitaxial layer, and the FWHM of $4cm^{-1}$ was obtained. This value is slightly different from the result of $3cm^{-1}$ obtained for the Si substrate. The difference may be due to the disordered region located near the sub-epi interface.

3.4 SIMS measurements

Figure 6 shows a boron profile as measured by SIMS. A photo-epitaxial layer was grown at $200^{o}C$ on a p^+ Si substrate with a boron concentration of $5x10^{18}cm^{-3}$. The boron concentration in the epitaxial layer was about $1.7x10^{15}cm^{-3}$, which is the detection limit of the SIMS system, and it was found that the auto-doping of boron was negligible. The transition distance from the sub-epi interface to the epitaxial layer is less than 500Å. The abrupt impurity profile of sub-epi interface is advantageous for the realization of VLSI devices.

3.5 Electrical properties

The electrical properties of epitaxial layers prepared from Si_2H_6 were evaluated by Hall measurements. The conduction type of an undoped epitaxial layer grown on a n-type 100Ωcm Si substrate at $200^{o}C$ was found to be n-type. The electron Hall mobility was measured by the Petritz's method[12] and showed a large value of $520cm^2/Vs$ with a low electron carrier concetration of $3.2x10^{14}cm^{-3}$. The n-type and p-type doping was carried out and the mobilities of epitaxial layers were measured by the van der Pauw Hall measurements. An epitaxial layer grown

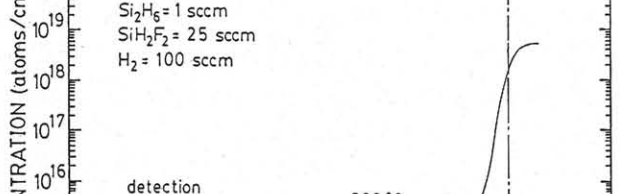

Fig.6 A boron profile measured by SIMS.

on a p^+ substrate with PH_3 doping gas showed n-type conduction with a carrier concentration of $1.3x10^{18}cm^{-3}$ and an electron mobility of $43cm^2/Vs$. An epitaxial layer grown on a n^+ substrate with B_2H_6 doping gas showed p-type conduction with a carrier concentration of $5.7x10^{17}cm^{-3}$ and a hole mobility of $27cm^2/Vs$. Further improvement in the electrical properties are expected by evacuating the photo-CVD system at ultra high vacuum (UHV) conditions and by cleaning the Si substrate with thermal treatment prior to the growth.

§4. Conclusions

We have grown Si epitaxial layers at a temperature as low as $200^{o}C$ and also succeeded in n-type and p-type doping using the mercury-sensitized photochemical vapor deposition technique. Furthermore, we have demonstrated that the presence of SiH_2F_2 in the gas phase is essential to the growth of Si epitaxy at this low temperature. RHEED, Raman scattering, SIMS and Hall measurements showed that the grown layers had good crystallinity.

Acknowledgements

The authors wish to thank Mitsu Toatsu Chemicals, Inc. for the supply of disilane and difluorosilane gases.

References

1) Y.Ota, J.Electrochem.Soc. 126, 1761 (1979)
2) M.J.P.Duchemin, M.M.Bonnetand and M.F.Koelsch, J.Electrochem.Soc. 125, 637 (1980)
3) T.J.Donahue and R.Reif, J.Appl.Phys. 57, 2757 (1985)
4) M.Kumazawa, H.Sunami, T.Terasaki and J.Nishizawa, Jpn.J.Appl.Phys. 7, 1332 (1968)
5) R.G.Frieser, J.Electrochem.Soc. 115, 401(1968)
6) T.Yamazaki, T.Ito and H.Ishikawa, Technical Digest of 1984 Symposium on VLSI Technology, San Diego, 1984, p.56
7) S.Nishida, H.Tasaki, M.Konagai and K.Takahashi, J.Appl.Phys. 58, 1427 (1985)
8) S.Nishida, M.Konagai and K.Takahashi, 46th Autumn Meeting of Japan Society of Applied Physics, Kyoto, 1985, preprint, p.728
9) S.Suzuki and T.Ito, J.Appl.Phys. 54, 1466 (1983)
10) A.Matsuda, Proceeding of the 10th International Conference on Amorphous and Liquid semiconductors, J.Non-Cryst.Solids 59&60, 767 (1983)
11) A.Matsuda, T.Yoshida, S.Yamasaki and K.Tanaka, Jpn.J.Appl.Phys. 20, L439 (1981)
12) R.L.Petritz, Phys. Rev. 110, 1254 (1958)