Process optimization and related material properties of silicon films produced by laser-induced chemical vapour deposition from silane

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Laser-induced chemical vapour deposition of silicon films on SiO_2/Si (1 0 0) and Si (1 0 0) substrates was studied using ArF laser irradiation of silane/argon gas mixture in parallel to the substrate. The optimal deposition conditions were specified by examination of film morphology at a wide range of irradiation and process parameters. At optimal conditions, specular films were obtained with no powder formation. The effect of deposition parameters, such as laser energy and repetition rate, on the deposition rate and the related film quality, was investigated.

1. Introduction

The specific use of silicon films depends on their microstructure and composition. For example, single crystals and polycrystalline silicon are used in integrated circuits [1], a: SiH is used for photovoltaic cells [2–4] and, recently, porous silicon has been considered for application in optical devices [5, 6]. Laser-induced chemical vapour deposition (LCVD) of silicon is a promising process, following the well-known CVD and plasma-enhanced CVD processes [7]. The main advantage of LCVD is the relatively low deposition temperature and low kinetic energy of decomposition products (several electron volts), hence the films produced have good quality, with sharp interfaces and with low internal stresses. LCVD of silicon has been reported, utilizing several types of lasers irradiating either perpendicular or parallel to the substrate in the environment of silane or disilane [8–16]. In the perpendicular mode of irradiation, CO_2 and argon lasers were mainly used to heat the substrate [8, 10]. In this case, the deposition mechanism is similar to the common thermal chemical vapour deposition [17]. In the parallel mode of irradiation, CO_2 or an excimer laser were used mainly to decompose the gas producing the compounds needed for film growth. This mode led to silicon deposition at relatively lower substrate temperatures (about 400 °C).

Recently, we have performed a systematic work studying the photochemical reaction in the gas phase during LCVD of silicon from silane as well as the growth kinetics [18, 19]. In this paper we present the results of process optimization showing the deposition conditions for obtaining good-quality silicon films and discuss the effect of the various parameters on the deposition rate and the related film properties.

2. Experimental procedure

A schematic drawing of the experimental system that was developed in our laboratory for laser-induced deposition is shown in Fig. 1. The deposition chamber was built from a stainless steel cylinder and had a volume of 25 l. Si (1 0 0) or SiO_2/Si (1 0 0) wafers (10 mm wide, 40 mm long), were used as substrates for the deposition. Silane gas, diluted with argon (15%), was introduced through a mass flow controller at a predetermined flow rate. The gas flow was directed upon the substrate through a few slits at the end of a tube. Argon gas was passed continuously in order to wash the entrance window to prevent deposition on it.

An ArF laser beam (20 mm × 5 mm) was directed into the chamber travelling in parallel either above or beside the substrate. The beam was concentrated using a focusing lens and its cross-section was 9×3 mm^2 and 6×2 mm^2, at the front and the rear edge of the specimen, respectively.

One of the main obstacles in the deposition process was the formation of a yellow powder in the gas phase leading to a deposition of a powdered film with poor adhesion to the substrate. The aim of the process optimization was to determine the maximum deposition rate at which both thermal deposition and powder formation did not take place.

The optimized range of values of each deposition parameter was determined on the basis of the film morphology, as observed by both optical and scanning electron microscopy (SEM). In the optimal range,

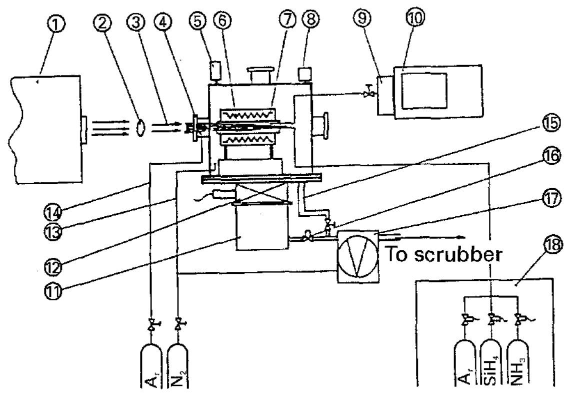

Figure 1 Schematic presentation of the LCVD system. 1, Laser; 2, focusing lens; 3, laser beam; 4, window; 5, Pirrani gauge; 6, specimen; 7, heater; 8, absolute pressure gauge; 10, mass spectrometer; 11, adsorption trap; 12, pneumatic valve; 13, N_2 line; 14, Ar purge; 17, vacuum system; 18, gas cabinet.

specular silicon films were formed. The morphology and microstructure of the deposited silicon films could be better analysed on SiO_2/Si than on silicon substrates and in this case ellipsometry measurements could be utilized as well. The effect of gas flow was studied by performing experiments at stagnant conditions and at flow rates between 20 and 50 standard $cm^3\,min^{-1}$ (SCCM). The ranges of the various deposition parameters that were studied are: total pressure 14–650 torr (1 torr = 133.322 Pa) substrate temperature 340–560 °C, laser energy 60–500 mJ cm^{-2}, laser repetition rate 10–27 Hz and distance between the laser beam and the substrate 1.5–6 mm. It was not possible to separate the effect of each parameter in all cases. Therefore, at the preliminary stage, more than one parameter was changed at the same time, whilst searching for the deposition of non-powdered silicon films. The minimal values of these parameters were chosen as the values where film growth could be observed after laser irradiation of 50 000 pulses. The deposition rate was evaluated from thickness measurements using alpha step and ellipsometry. The microstructure of good-quality films was studied by transmission electron microscopy (TEM) of cross-sectional samples. The film composition was studied using Auger Electron Spectroscopy (AES) and hydrogen and argon concentrations were determined by Secondary Ion Mass Spectroscopy (SIMS). The film morphology was studied by scanning electron microscopy (SEM).

3. Results and discussion

As was stated in Section 2, one of the major problems in the process of optimization of the deposition parameters was the formation of a powdered silicon film. This phenomenon, which is a result of a homogeneous nucleation in the gas phase, occurred whenever we tried to increase the deposition rate.

The formation of powdered films was manifested in the morphology of the films as observed in the scanning electron micrographs shown in Fig. 2. These micrographs correspond to films deposited at different substrate temperatures under stagnant conditions, namely when no gas flow occurred during deposition. The deposition conditions of these films were found to

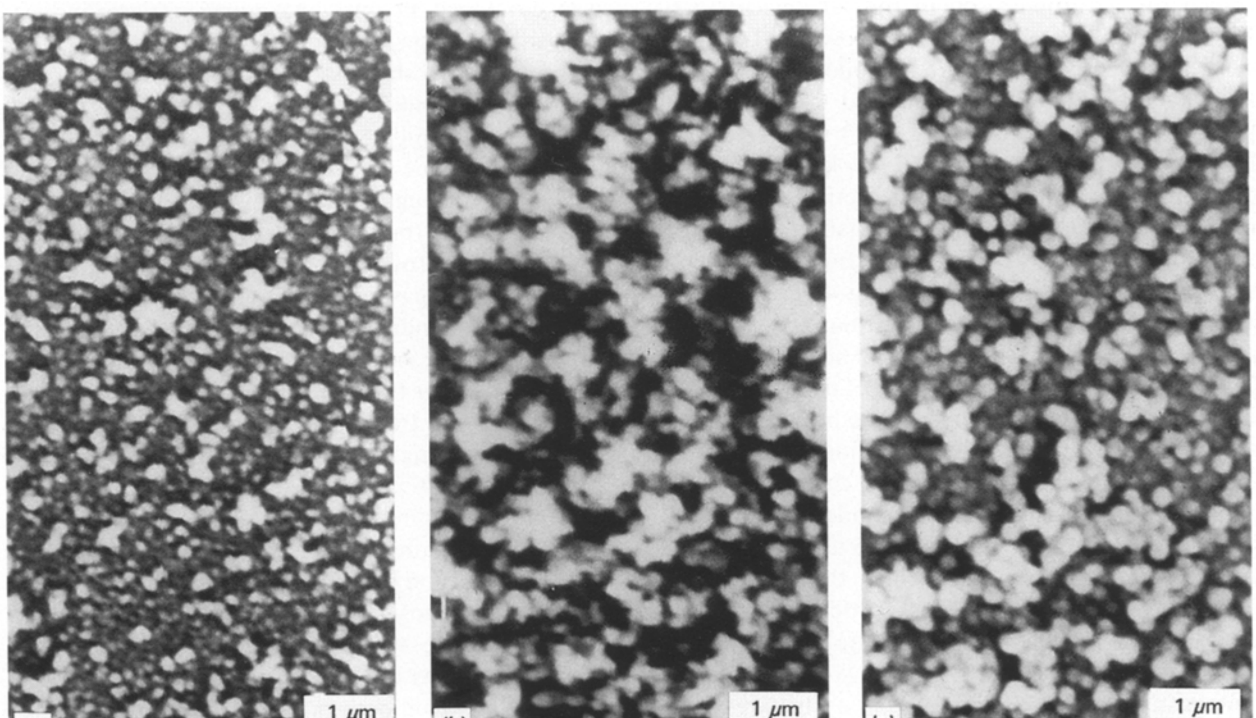

Figure 2 Scanning electron micrographs of silicon film deposited by laser irradiation under stagnant conditions and high pressure. Deposition conditions: (a) temperature 664 °C, total pressure 101 torr, laser energy 60 mJ cm^{-2}, repetition rate 10 Hz, 20 000 pulses; (b) temperature 664 °C, total pressure 584 (122) torr, laser energy 60 mJ cm^{-2}, repetition rate 10 Hz, 20 000 pulses; (c) temperature 657 °C, total pressure 190 torr, laser energy 100 mJ cm^{-2}, repetition rate 10 Hz, 5000 pulses.

be outside the region of optimum values for deposition, but they are shown here because they exhibit the film morphology during powdered deposition. As can be seen, the films have a rough structure caused by the deposition of large solid particles of silicon. The particles dimensions are about 1 μm.

X-ray diffraction analysis of powdered film showed that polycrystalline silicon was grown, even at a low substrate temperature (400 °C). These particles may also contain polyatomic molecules of silane derivatives, as was observed elsewhere [14]. During laser irradiation when the powder films were formed, an illumination was observed in the gas in the beam path. The source of illumination was not analysed; however, it was similar to the glow discharge that is observed during plasma-enhanced CVD. Powdered films were obtained also in a continuous gas flow of 50 standard SCCM. However, for this flow we could also find a range of parameters where specular films were obtained. Further decrease of the flow rate to 20 standard SCCM led to a deposition of films of better quality, and no powder was observed in a wide range of deposition conditions. Scanning electron micrographs of good-quality films (where no powder was observed), are shown in Fig. 3. It can be seen, that the surface morphology is much finer than that of the films shown in Fig. 2. The particles on the surface are small, and at the optimized deposition conditions no features are observed at a magnification of 25 000 (Fig. 3c). By using mass spectrometry for gas-phase analysis, it was found that during the strong gas-phase reaction, when heavy powder was formed, silicon atoms were not detected, in contrast to the case where a good film was grown. This could be explained as silicon cluster formation in the gas phase which could not reach the mass spectrometer detector.

As stated previously [19] and also by others [20], the silane molecule was found to dissociate by a two photon absorption mechanism. As a consequence, the dissociation efficiency should be rather low; therefore, in order to get a reasonable deposition rate, the total amount of silane should be increased. Increasing the gas pressure is followed by a decrease of the mean free path of the molecule, leading to an increase of the probability for collision between silane derivatives and other gas molecules, resulting in cluster formation. The mean free path calculated for argon atoms, which is the major constituent of the gas mixture, is 0.7 μm at 60 torr, which was the maximum pressure utilized in optimized deposition conditions. This value is much smaller than the distance of the beam from the substrate which was in order of millimetres. Therefore, during laser irradiation, the silane derivatives which are produced must be transferred towards the substrate in a time shorter than the time between collision with other atoms or molecules in the gas phase. It is, therefore, more beneficial to decrease the flow rate and the pressure. For this reason it seemed that the argon gas used for dilution has a negative effect by decreasing the maximum deposition rate which is possible, even though it was found by other authors that argon and helium gases are important for initiation of the deposition [21].

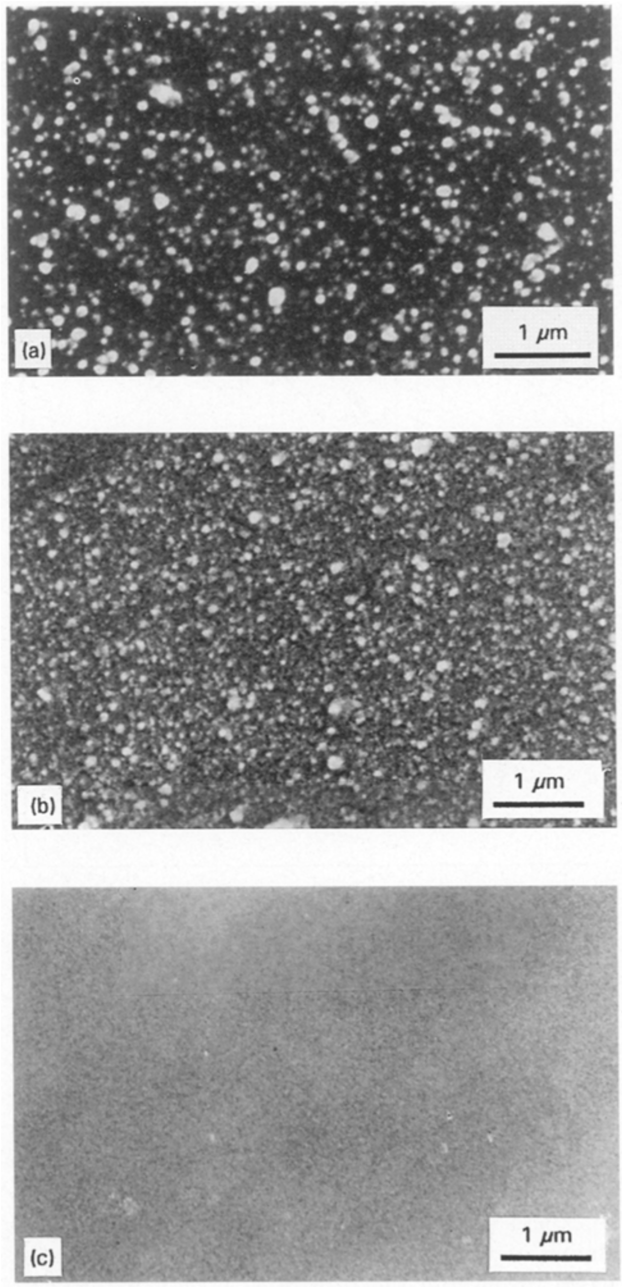

Figure 3 Scanning electron micrographs of silicon films deposited at continuous flow and high pressure. Deposition conditions: temperature 380 °C, total pressure 61 torr, laser energy 166–183 mJ cm^{-2}, 50 000 pulses. (a) Repetition rate 20 Hz, distance between beam and specimen 6.5 mm; (b) repetition rate 10 Hz, distance between beam and specimen 5.5 mm; (c) repetition rate 20 Hz, distance between beam and specimen 2.5 mm.

The evaluation of the optimal deposition parameters was based on thickness measurements and calculations of the deposition rate when no powder was observed. It was found that this can be better achieved by deposition on a SiO_2/Si substrate because the silicon film has a different refractive index from the SiO_2, resulting in a film colour which depends on its thickness. Therefore, the film quality could be evaluated immediately after deposition simply by visual inspection. In this way it was found that films deposited under specific conditions always exhibited a variation in colours due to a variation in inhomogeneous thickness. Measurement by ellipsometry showed that a transverse thickness distribution was observed in

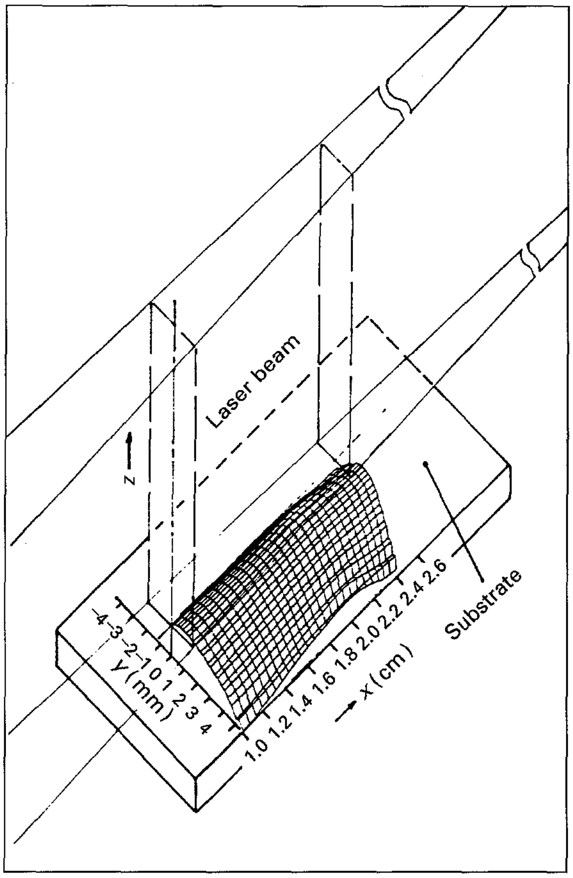

Figure 4 Thickness distribution at three dimensions of silicon film. Deposition conditions: silane/Ar flow rate 20 standard $cm^3 min^{-1}$, total pressure 14 torr, laser energy 257 $mJ cm^{-2}$, repetition rate 15 Hz, 50 000 pulses.

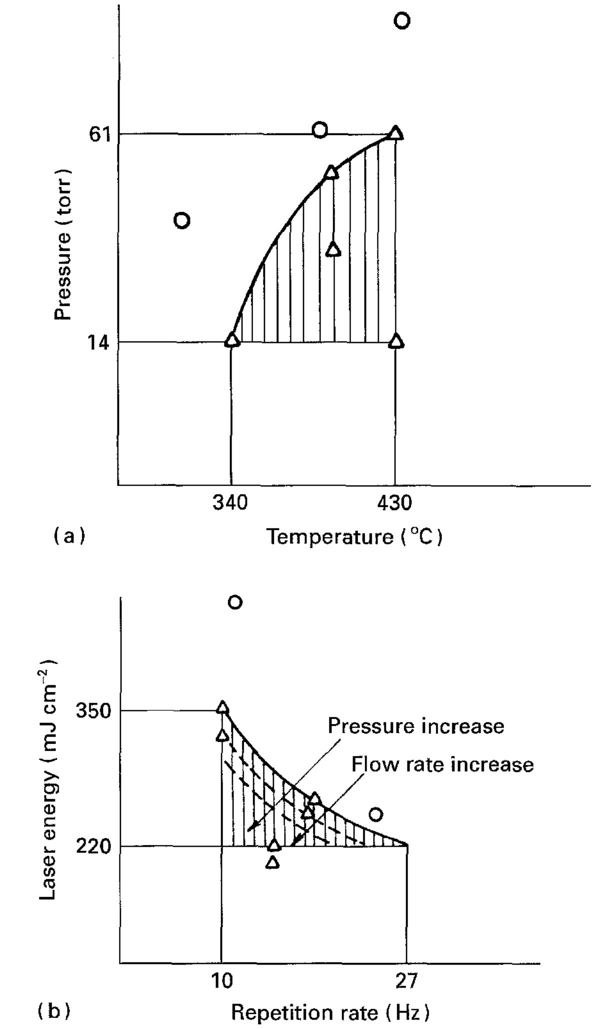

Figure 5 Optimized range of values of (a) total pressure and substrate temperature, for laser-induced deposition of silicon, and (b) laser intensity and repetition rate.

a direction perpendicular to the direction of the beam propagation. The thickness remained almost constant along the propagation axis of the laser beam, up to a certain pressure (250 torr) where a large absorption in the gas has occurred. A typical result of the film-thickness distribution is illustrated in Fig. 4. Also shown in the figure is the orientation between the beam image and the substrate. A plot of thickness distribution in the transverse direction could be fitted to a gaussian distribution, and the deposition rate was computed at the point of maximum thickness.

Fig. 5 shows schematic drawings of the range of optimized values of parameters for silicon deposition in two different cuts. Fig. 5a describes the optimum values of process parameters and Fig. 5b those of irradiation parameters. The dashed area in each scheme is the range in which specular films were obtained, and the actual corresponding experiments are also marked (△); powdered films are also indicated (○). Fig. 5a shows that the optimal range of temperatures and pressures are 340–430 °C and 14–61 torr, respectively. A pressure increase must be followed by a substrate temperature increase in order to prevent powder formation, and for higher temperatures the range of optimized pressure is extended. As mentioned above, minimal values of pressure and temperature were determined as the minimum deposition conditions where a silicon film could be observed after total irradiation of 50 000 pulses. The maximal temperature was determined as the threshold temperature for thermal deposition. Increasing the substrate temperature above this temperature gradually decreased the contribution of the laser for the deposition rate; above an ultimate temperature of 560 °C the laser contribution could be neglected, and practically all the deposition occurred only due to thermal decomposition of the silane. Fig. 5b shows the range of optimal values of laser energy and repetition rate. An increase in the repetition rate must be followed by a decrease of the laser energy in order to keep the decomposition rate of the silane at the same value where the probability for powder formation is low. The dashed lines in the figure show that the optimized region is shrunk with the increase in pressure or flow rate.

At a laser irradiation energy of 300 $mJ cm^{-2}$, within the range of optimized conditions, no significant change in the film thickness was observed on increasing the repetition rate between 10 and 20 Hz, and the measured thickness obtained after 50 000 pulses was about 10 nm (Fig. 6a). For higher rates, the thickness decreased, probably because the gas decomposition rate was above a critical value where the powder is formed. Therefore, in order to increase the apparent deposition rate, it is useful to work at a deposition rate of 20 Hz (Fig. 6b). The maximal deposition rate at the optimized deposition condition was 1.3 $nm min^{-1}$.

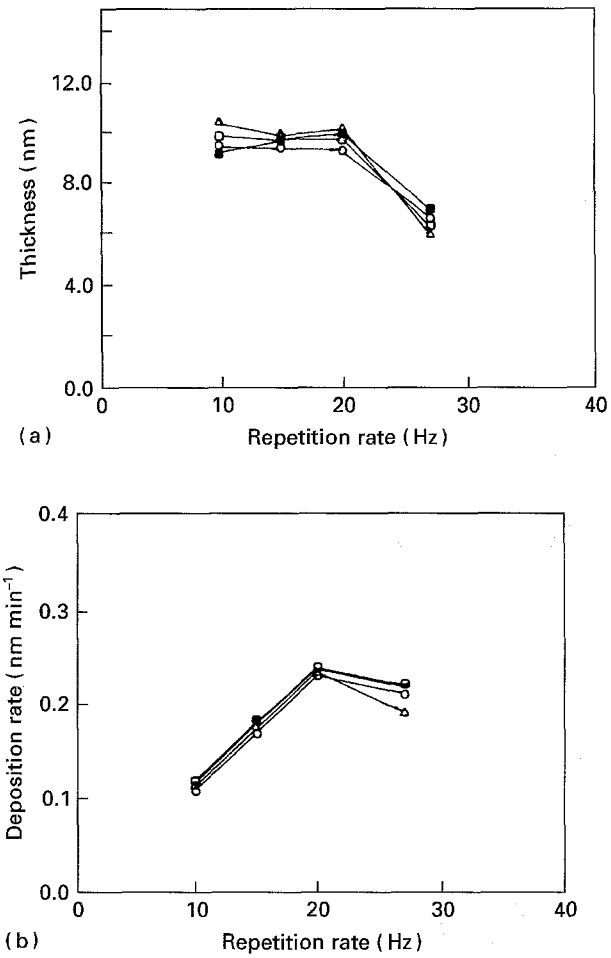

Figure 6 (a) Film thickness and (b) silicon deposition rate versus laser repetition rate. Deposition conditions: silane/Ar 20 standard $cm^3 min^{-1}$, substrate temperature 430 °C, laser intensity 300 $mJ cm^{-2}$, 50 000 pulses along the specimen. (△) 1 cm, (□) 2 cm, (■) 3 cm, (○) 4 cm.

This value was obtained at a flow rate of 20 standard $cm^3 min^{-1}$, a total pressure of 61 torr (silane pressure 9.15 torr), a repetition rate of 15 Hz, a laser energy of 300 $mJ cm^{-2}$, and a substrate temperature of 430 °C. It should be noted that according to the results discussed above, there was still a possibility to increase the deposition rate without the formation of powdered film by increasing the repetition rate to 20 Hz, by a factor of 20/15, which is the ratio between the two values of repetition rates.

The maximal values of deposition rate in our study were lower by more than one order of magnitude from the value of 35 $nm min^{-1}$ found by Bilenchi *et al.* [22] using a CO_2 laser for irradiation at an intensity of 250 $W cm^{-2}$ of silane at 4.35 torr (SiH_4/N_2 total pressure of 10 torr) at a flow rate of 5.75 standard $cm^3 min^{-1}$ and 320 °C. Meunier *et al.* [14] obtained a maximal deposition rate of 16 $nm min^{-1}$ using the same laser and irradiation of pure silane at 330 $W cm^{-2}$.

The much lower deposition rates in our work compared to CO_2 irradiation apparently are surprising because a higher efficiency of dissociation is expected using an excimer laser with a higher photon energy than the CO_2 laser and the mechanisms of laser/gas interaction are completely different in both cases. Using an excimer laser operating at 193 nm (6.4 eV) the silane gas is believed to undergo molecular dissociation by two-photon absorption, following excitation of the electronic states. On the other hand, the low value of photon energy (0.12 eV) obtained from the CO_2 laser is absorbed through vibrational excitation followed by a thermal relaxation of the molecule [17]. This result can be explained by assuming that the growth-rate limiting step is mass transfer and not the dissociation of the gas molecule. This assumption was verified by the result that the deposition rate remained almost constant at laser energies of 160–300 $mJ cm^{-2}$. The lower values of deposition rate found in our work can also be explained by the fact that this is an apparent deposition rate, calculated by dividing the thickness by the total time without considering the fact that the irradiation is in pulses of a very short time. Actually, the gas decomposition occurs during the duration of the pulse which is 24 ns and so the rate of photon supply is 10^{24} $ph s^{-1}$ for each laser pulse which is supplied for a very short time compared to 10^{21} $ph s^{-1}$ supplied continuously for longer time in the other works. The work in a pulsed mode of laser irradiation lead to high decomposition rate and increased the probability to cluster formation due to molecular collision, which therefore can be eliminated by mass transfer control.

Transmission electron micrographs of a cross-sectional view and the corresponding diffraction patterns of as-deposited silicon film and after heat treatment at 950 °C for 30 min, are shown in Fig. 7a and b. The film was deposited on SiO_2/Si (1 0 0) at a substrate temperature of 430 °C, a flow rate of 20 standard $cm^3 min^{-1}$, a total pressure of 61 torr, a laser energy of 257 $mJ cm^{-2}$, a repetition rate of 15 Hz, and a total of 285 000 pulses. The deposition conditions were in the range of the optimal values of the parameters and the number of pulses was increased in order to obtain a thick film easier for characterization. A dark-field image using a (1 1 1) reflection of the polycrystalline diffraction pattern at the annealed state, is shown in Fig. 7c. As shown in these pictures the thickness of the deposited silicon film is 80 nm, it is amorphous in the as-deposited state and it has recrystallized into polycrystalline silicon after the heat treatment. The interface between the silicon film and the substrate is sharp and no interaction between the deposited film and the substrate has occurred. Similar microstructures and diffraction patterns were obtained for films deposited at the same substrate temperature and gas flow rate, in a pressure range of 14–250 torr. However, at 250 torr the upper surface of the film was no longer flat and some clusters were observed. Laser-intensity changes in the range of 160–250 $mJ cm^{-2}$ had no effect on the film microstructure, and no significant difference in thickness was observed.

The composition of the film shown in Fig. 7a was analysed by Auger Electron Spectroscopy, and the corresponding spectrum after argon ion sputtering of 80 nm is shown in Fig. 8. The film contains traces of carbon and oxygen in a concentration lower than 1%. These impurities were found in smaller amounts in a film which was deposited at a total pressure

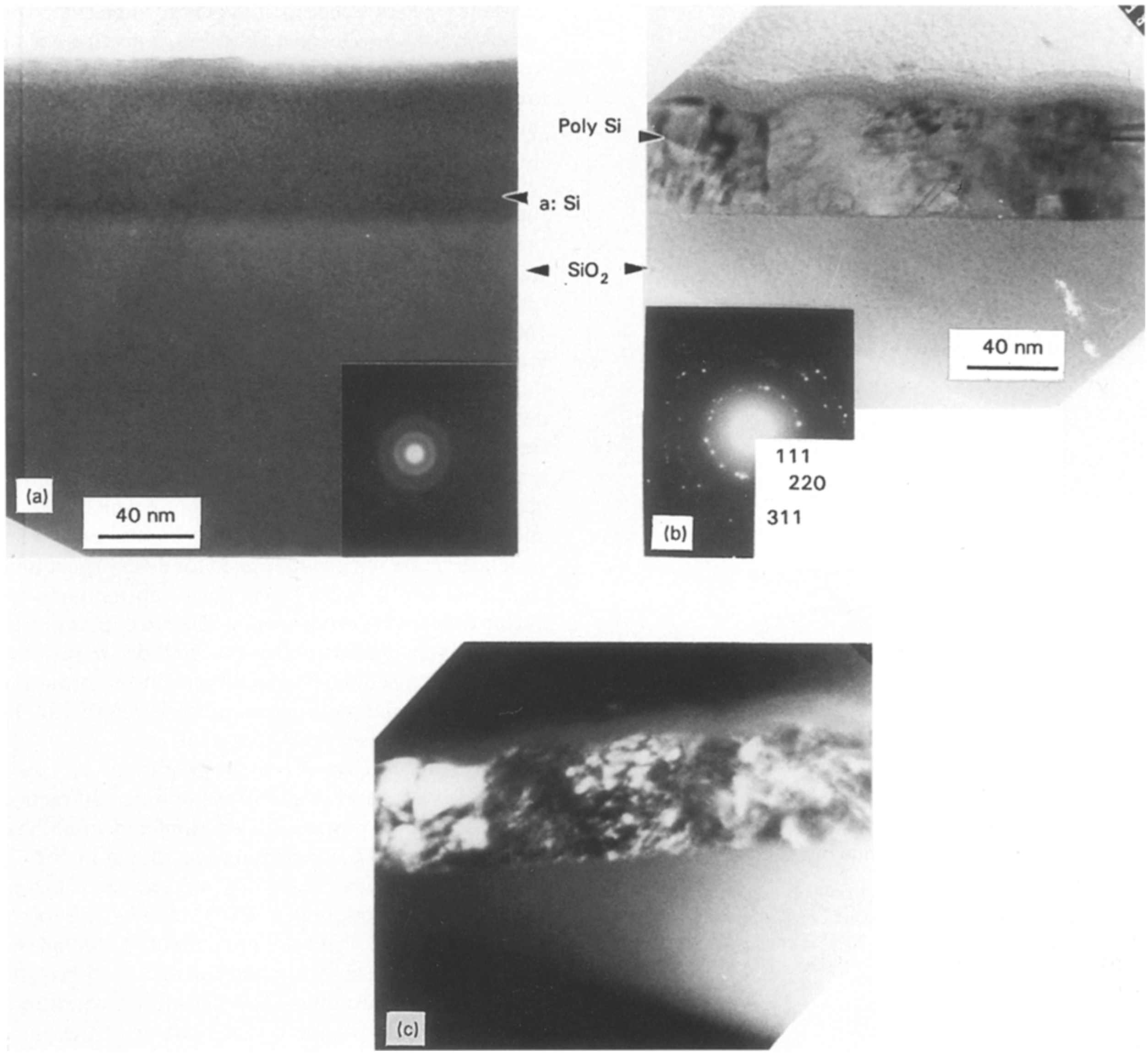

Figure 7 Transmission electron micrograph and microdiffraction pattern of cross-sectional view of a silicon film deposited on SiO_2/Si at a vertical configuration. Deposition conditions: silane/Ar flow rate 20 standard $cm^3\ min^{-1}$, total pressure 61 torr, temperature 430 °C, laser energy $257\ mJ\,cm^{-2}$, repetition rate 15 Hz, 280 000 pulses, (a) Before heat treatment, (b) after heat treatment, (c) dark-field image of B.

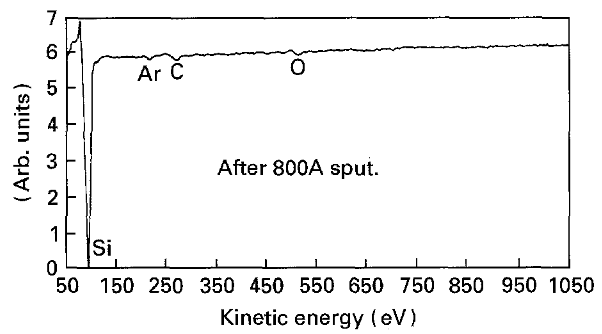

Figure 8 Composition of elements observed by Auger electron spectroscopy of a silicon film deposited on SiO_2/Si at vertical configuration. Deposition conditions: silane/Ar flow rate 20 standard $cm^3\ min^{-1}$, total pressure 61 torr, temperature 430 °C, laser energy $257\ mJ\,cm^{-2}$, repetition rate 15 Hz, 280 000 pulses.

of 14 torr. The hydrogen concentration in the film as obtained by SIMS analysis (Fig. 9) is 4×10^{20} atoms cm^{-3} which is 0.8%. The hydrogen amount was lower (0.4%) in a film deposited at 14 torr. This concentration is very low compared to silicon deposition by a CO_2 laser irradiating silane or disilane [23].

4. Conclusions

Silicon thin films were grown on Si (1 0 0) and SiO_2/Si (1 0 0) substrates using an ArF laser irradiating parallel to the substrate. The optimal range of parameters for deposition was specified according to film quality and deposition rate. Good-quality films were characterized by smooth morphology with a cluster size of less than 0.1 µm. These films had good spectral reflectance in the visible range and their thickness could be measured by ellipsometry. The optimized range was limited by powder formation in the gas phase and on the substrate. The silicon films were amorphous in the as-deposited form, and contained oxygen, carbon and hydrogen in amounts less than 1%.

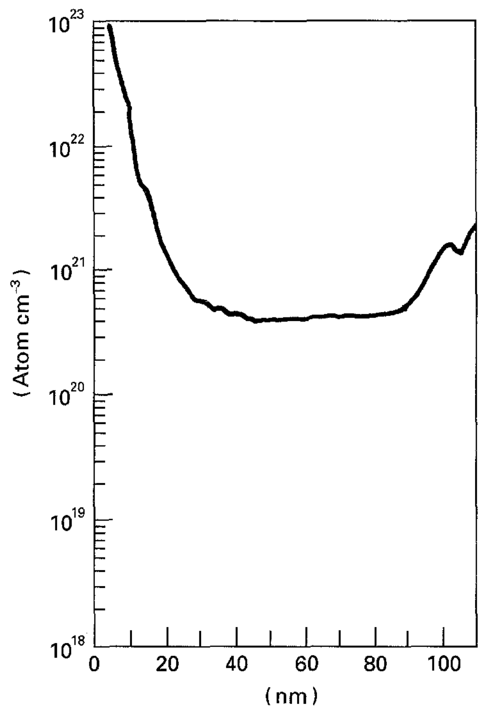

Figure 9 Hydrogen concentration profile of silicon film deposited on SiO_2/Si at vertical configuration. Deposition conditions: silane/Ar flow rate 20 standard cm^3 min^{-1}, total pressure 61 torr, temperature 430 °C laser energy 257 mJ cm^{-2}, repetition rate 15 Hz, 280 000 pulses.

References

1. S. M. SZE, "VLSI Technology", 2nd Edn (McGraw-Hill, NY, USA, 1988).
2. A. ROTH and F. J. COMES, *J. Non-Cryst. Solids* **137** (1991) 721.
3. J. D. JOANNOPOULOS and G. LUCOVSKY, *Topics Appl. Phys.* **55** (1984) 56.
4. M. KONAGI, *Mater. Res. Soc. Symp. Proc.* **70** (1986) 257.
5. Y. OCHIAI, N. OOKUBO, H. WATANABE, S. MATSUI, Y. MOCHIZUKI, H. ONO, S. KIMURA and T. ICHIHASHI, *Jpn J. Appl. Phys.* **31** (1992) 1560.
6. L. T. CANHAM, *Appl. Phys. Lett.* **57** (1990) 1046.
7. B. A. SCOTT, R. M. PLECENIK and E. E. SIMONYI, *ibid.* **39** (1981) 73.
8. C. P. CRISTENSEN and K. M. LAKIN, *ibid.* **32** (1978) 819.
9. D. J. EHERLICH, R. M. OSGOOD Jr and T. F. DEUTSCH, *ibid.* **39** (1981) 166.
10. D. BAUERLE, P. IRSILGER, G. LEYENDECKER, H. NOLL and D. WAGNER, *ibid.* **40** (1982) 819.
11. A. ISHIZU, Y. INOUE, T. NISHIMURA, Y. AKASAKA and H. MIKI, *Jpn J. Appl. Phys.* **25** (1986) 1830.
12. G. AUVERT, T. TONNEAU and Y. PAULEAU, *Appl. Phys. Lett.* **52** (1988) 1062.
13. M. HANABUSA, *J. Non-Cryst. Solids* **59, 60** (1983) 703.
14. M. MEUNIER, J. H. FLINT, S. HAGGERTY and D. ADLER, *J. Appl. Phys.* **62** (1987) 2812.
15. P. HESS, *Spectrochim. Acta* **46A** (1990) 489.
16. S. LIAN, B. FOWLER, D. BULICCK and S. BANERJEE, *Appl. Phys. Lett.* **58** (1991) 514.
17. K. HESCH, H. KARSTENS and P. HESS, *Thin Solid Films* **218** (1989) 29.
18. S. TAMIR, Y. KOMEM, M. EIZENBERG and J. ZAHAVI, E-MRS Symposium F Spring Meeting, Strassbourg, France, May 1993.
19. S. TAMIR, Y. KOMEM, M. EIZENBERG and S. SPIESER, *SPIE* **2017** (1993) 208.
20. E. BOCH, C. FUCHS, E. FOGARASSY and P. SIFFERT, *Mater. Res. Soc. Symp. Proc.* **129** (1989) 195.
21. T. R. DIETRICH, S. CHIUSSI, H. STAFAST and F. J. COMES, *Appl. Phys. A* **48** (1989) 405.
22. R. BILENCHI, I. GIANINONI and M. MUSCI, *J. Appl. Phys.* **53** (1982) 6479.
23. A. YAMADA, M. KONAGAI and K. TAKAHASHI, *Jpn J. Appl. Phys.* **24** (1985) 1586.

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