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Ultra-low pressure chemical vapour deposition of polycrystalline and amorphous silicon

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The deposition of undoped polycrystalline and amorphous silicon in an ultra-low pressure chemical vapour deposition system capable of achieving operating pressure of 0.03 Pa is discussed. It is found that at deposition temperatures in the region of 630 °C and reactor pressures of less than 1.3 Pa very large grained polycrystalline silicon films are obtained, and in this regime the growth rate is independent of the reactor pressure. Excellent uniformity is obtained and the process can be easily scaled up for large substrates and high volume batch production.

1. Introduction

Low pressure chemical vapour deposition (LPCVD) of polysilicon is widely used in integrated circuit fabrication processes, mainly for gate electrodes and interconnects [1]. As the material is subsequently doped and recrystallized, the morphology of the as-deposited film is not of primary importance [2, 3]. Therefore, the deposition parameters are chosen to optimize the reactor throughput for high deposition rates and uniformity over a large number of substrates simultaneously [4]. For several emerging technologies, chiefly large-area displays and multi-layer memories, the crystalline quality of the as-deposited layer is of paramount importance as the material is the active semiconductor layer in the electronic device. For these applications it is important to lower the deposition temperature as much as possible to avoid damage either to the substrate or circuit elements already present [5, 6].

In this paper we shall demonstrate that the morphology of the as-deposited polysilicon films, using silane in the temperature range 580–630 °C, is very closely related to the deposition parameters, particularly the system pressure. This work is a consequence of the observation that under standard LPCVD conditions, the amorphous–polycrystalline transition occurs at around 590 °C whereas it occurs at 675 °C for depositions at atmospheric pressure [7]. It is expected that a reduction in pressure from typical LPCVD pressures (around 26.6 Pa) will cause the transition temperature to be lowered, allowing a crystalline film to be grown at a relatively low temperature. To achieve this, a special LPCVD system has been constructed to investigate layer growth at pressures down to 0.03 Pa. Similar results have been obtained in a large area commercial system now manufactured by Rytrak Ltd.

Polysilicon thin film transistors fabricated in the resulting materials exhibit much improved performance and have been fully reported elsewhere [8]. When this work was completed, Meyerson *et al.* [9] presented results on a low temperature epitaxial system of a similar design. The work discussed here is complimentary as it not only presents new results on the structural properties of polysilicon films but also yields important data on the fundamental limits at which epitaxial growth can be achieved. The dependence of film morphology on the deposition rate, gas flow rate and reactor temperature is discussed.

2. Experimental procedure

Fig. 1 shows a schematic of the ultra-low pressure CVD reactor used for this work. Up to fifty 75 mm diameter wafers are held vertically in a quartz wafer boat within a fused silica tube of 96 mm internal diameter. This was heated by a conventional resistance heater (furnace) which gave process temperatures uniform to within ± 1 °C over the hot zone. A 250 m h^{-1} Roots-rotary combination was used to rough the chamber, this combination also allowed experiments to be carried out at conventional pressures. For very low pressure experiments, a 3601 s^{-1} turbomolecular pump backed by a 30 m h^{-1} rotary pump was used. This was isolated from the main

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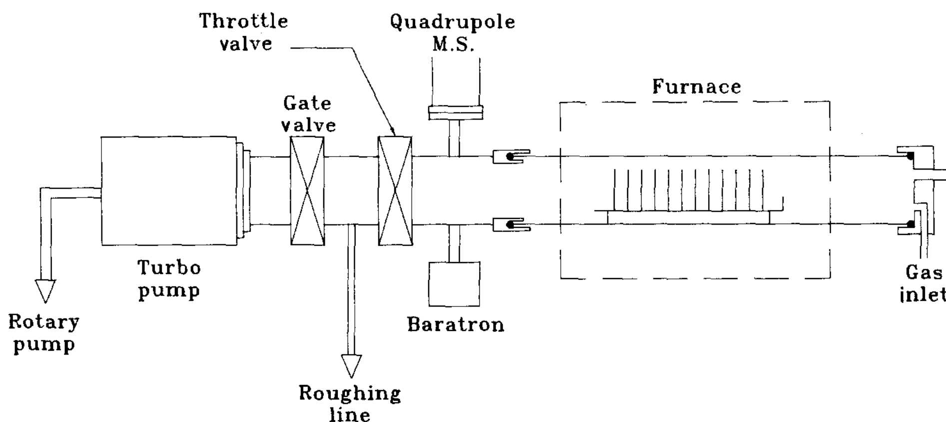

Figure 1 Schematic of the UHV–CVD reactor.

system by a gate valve and an automatic feedback-controlled throttle valve for independent pressure control. The process pressure was measured at the exhaust end of the tube by a capacitance manometer (MKS) which was accurate to better than 1% in the pressure range considered (0.03–24 Pa). The pressure readings from this gauge head were initially calibrated using a separate gauge located at the load end of the reactor tube. The gauge was zeroed prior to each deposition by pumping to less than 1.33×10^{-4} Pa and the stability was assisted by the gauge never being subjected to more than 66.6 Pa at any one time. The process gas (100% silane) was admitted to the chamber *via* a system of valves and a low flow mass flow controller (MKS or PFD). Precision electronics and a controlled environment were used to ensure stability and reproducibility of flow.

For these experiments 75 mm diameter thermally oxidized silicon wafers were chemically cleaned and loaded into the wafer boat at preset slot positions; the remaining slots were filled with dummy wafers. After placing the wafer boat into the reactor tube, the system was pumped with the turbomolecular pump for 30 min to allow the wafer temperature to stabilize. At this point the base pressure, without baking the stainless steel vacuum lines, was less than 1.33 $\times 10^{-4}$ Pa. Baking was not felt to be necessary due to the repeated venting of the system for loading and unloading. However for epitaxial deposition of silicon at low pressures the vacuum quality requirements have to be much stricter to prevent oxidation of the silicon wafers prior to deposition [9]. Silane was admitted to the chamber at the desired flow rate and the throttle valve activated to obtain the correct process pressure. In the case of deposition at 26.6 Pa, a changeover to the Roots pump was effected and the pressure controlled by a throttle valve in the Roots pump line.

After deposition, the chamber was evacuated to less than 1.33×10^{-4} Pa and backfilled with inert gas prior to removal of the test wafers. Films in the thickness range 0.2–1.5 micrometres were grown, this covers both the thickness range used in thin film transistors, TFTs, (around 0.3 micrometres) and allows inspection of much thicker films to further elucidate effects observed in thinner films. Polysilicon films were grown in the temperature range 580–630 °C with the silane flow rates of 0.5 to 5.0 sccm and pressures ranging from 0.03–24 Pa. With the exception of a few films which exhibited a rough surface, the films showed excellent uniformity and homogeneous morphology. Thicknesses were measured with a surface profilometer or an optical thickness monitor and the results compared with those obtained from cross-sectional transmission electron microscopy (TEM) experiments. Detailed structural analysis was obtained using TEM and cross-sectional TEM, electron diffraction techniques and combined ultraviolet (u.v.) reflectance was used to characterize the film surface.

3. Results and discussion

3.1. Deposition rate

Oxidized silicon test wafers were placed at equal spacings down the length of the boat in order to measure the growth rate of polysilicon. Dummy wafers were placed before the first test wafers to allow the precursor gas to reach the desired temperature and the flows to adjust to the geometry of the wafers and boat. The growth rates shown are extrapolated back from the wafer in the zeroed slot position in the manner of previous workers for comparison [10]. Fig. 2 shows the growth rate as a function of the total

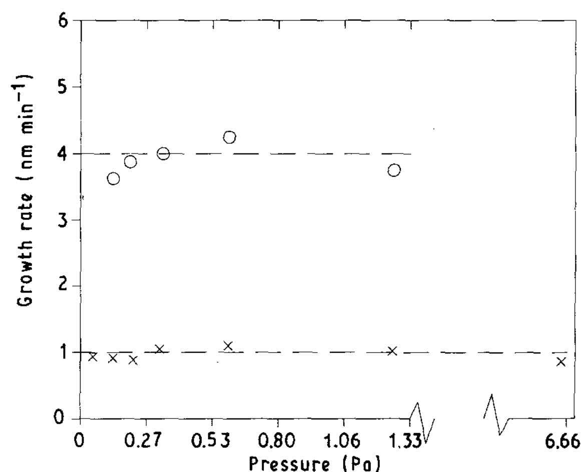

Figure 2 Deposition rate as a function of pressure at 630 °C for films grown at (×) 1 and (○) 5 sccm.

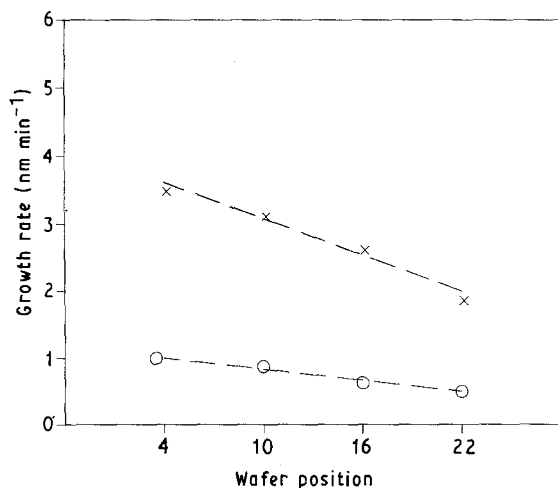

Figure 3 Deposition rate as a function of axial wafer position for total pressure of 0.66 Pa (○) 1 and (×) 5 sccm of silane.

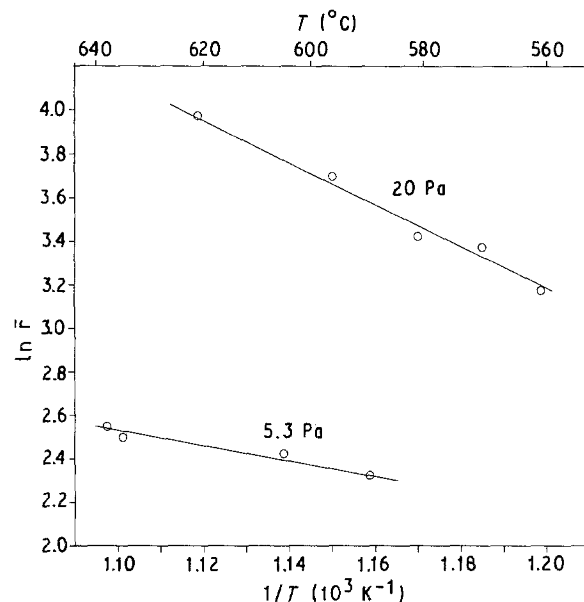

Figure 4 Log deposition rate versus reciprocal temperature for pressures of 20 and 5.3 Pa.

pressure at 630 °C with silane flow rates of 1 and 5 sccm. It can be seen that the deposition rate is unaffected by the total system pressure under these conditions. This is in direct contrast to recent results obtained from a cold-wall epitaxial reactor [11] but it is not clear whether this is due to the horizontal configuration in the above system or a consequence of the cold-wall reactor. Several workers have suggested that under typical LPCVD conditions the silane decomposes into SiH_2 in the gas phase and may recombine with silane to form disilane (Si_2H_6). In our investigations, residual gas analysis using a quadrupole mass spectrometer, showed that no disilane was present in the gas phase. Moreover, the radial uniformity of the deposition rate on the wafers was better than 0.5%. Hence the parent molecule is silane which may decompose into SiH_2 on the wafer surface. Purnell and Walsh [12] showed homogeneous pyrolysis of silane occurs but under conditions very different from those investigated here and therefore the mechanisms of growth are also likely to be very different. This is supported by the results showing that the presence of disilane in the gas phase results in non-uniform deposition rates radially across the wafer [13, 14].

Fig. 3 shows the deposition rate as a function of wafer position in the wafer boat for gas flows of 1 and 5 sccm with the total system pressure of 0.66 Pa. For both gas flows investigated, the deposition rate decreased from wafer 1 to wafer 25 by a factor of two due to the depletion of silane as it is consumed along the length of the reactor tube. However the deposition rate at a silane flow of 5 sccm is 4–5 times greater than that obtained at 1 sccm. For standard LPCVD conditions the deposition rate has been observed to increase linearly for low flow rate and then saturate at higher flows [10] and a similar explanation would be applicable in this case. At low flow rates the surface of the wafers is deficient of silane with many free active sites onto which silane or it's products can adsorb. As the flow rate is increased these sites become filled and eventually saturated and thus the deposition rate follows the same trend.

The temperature dependence of the deposition rate for the zeroed wafer is shown in Fig. 4 for two different pressures. For 20 Pa, the apparent activation energy is calculated to be 209 kJ mol^{-1}. Fig. 4 is indicative of the deposition rate controlled by a surface phenomenon rather than by a gas phase process. When the system pressure was lowered to 5.3 Pa the apparent activation energy was calculated to be 159 kJ mol^{-1}. In this experiment the pressure was lowered by reducing the gas flow rate from 60 to 12 sccm. At this low flow rate it may be concluded that the reduction of the activation energy is not due to a change in the rate determining surface process but is an artifact of the reduced supply of silane precursor to the surface. For the deposition rate to increase with temperature, more silane must be supplied to the surface. This experiment needs to be repeated at different pressures with gas flow rates being kept constant. It has been shown that for a cold-wall single wafer reactor in the temperature range of 600–675 °C the activation energy is independent of pressure [11].

3.2. Film structure

The effect of the total reactor pressure on the film structure was studied at a constant growth temperature of 630 °C. This is of practical importance as it is near to the highest tolerable temperature for the processing of glass substrates. Additional runs were made at lower temperatures to confirm the general trends seen. Recent work by another group agrees well with what we have found [15].

3.2.1. Conventional pressures

All films deposited at pressures in the region of 26.6 Pa exhibited a microcrystalline structure, although the average crystallite size increased with film thickness, agreeing with the measurement obtained from TFT's made from such films [16]. The crystallites have a 'V' shape appearance starting from the bottom interface with a mean angle of 15° to the normal and are heavily

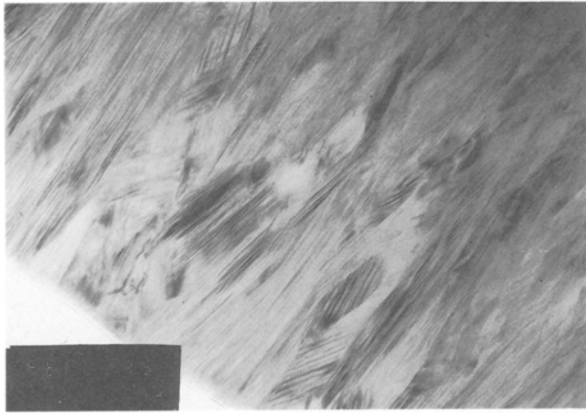

Figure 5 Cross-sectional TEM micrograph for a film deposited at 630 °C and 24 Pa.

striated with thin laminar ⟨1 1 1⟩ microtwins ranging in thickness from 2–20 nm. Fig. 5 which is a cross-sectional TEM of a film deposited at 24 Pa and 630 °C shows this clearly and the corresponding diffraction pattern, Fig. 6, shows parallel streaks compatible with the observation of microtwinning. A perpendicular view of the film is shown in Fig. 7. The corresponding

Figure 6 Electron diffraction pattern for a film deposited at 630 °C and 24 Pa.

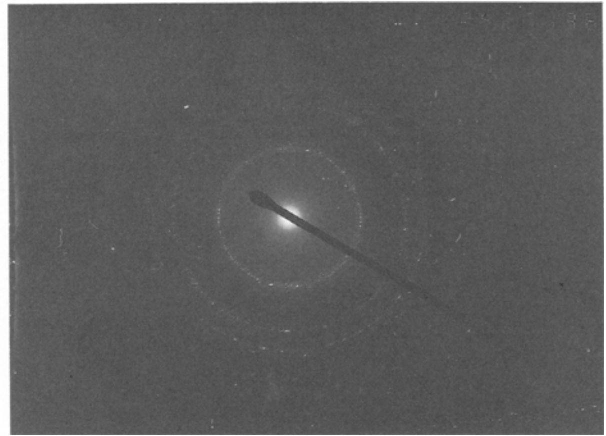

Figure 8 Electron diffraction pattern for a film deposited at 630 °C and 24 Pa.

electron diffraction pattern, Fig. 8, is shown with a characteristically strong ⟨1 1 1⟩ diffraction ring, consisting of individual spots with a radial dispersion. Comparison with the diffraction from the silicon substrate results in a dispersion of the lattice constant of 3%, indicating a compressive or dilational strain. This effect, which is always seen in our films deposited at conventional pressures, is of utmost importance in devices exploiting the field effect, as the band structure of the material will be seriously effected by the lattice constant dispersion.

3.2.2. *Intermediate pressures*

In this range of pressures the degree of microtwinning is depressed, as is evident from the diffraction pattern shown in Fig. 9 for material deposited at 6.66 Pa. The streaking seen in Fig. 6 and 8 is no longer present. However the elongated appearance of the grains perpendicular to the substrate persists. A cross-sectional TEM of a film deposited at 6.66 Pa is shown in Fig. 10, the grains in this case are entirely columnar. No lattice constant dispersion is observed at this pressure, suggesting that devices of improved performance may be obtained from this material. This was found to be the case, indicating that this pressure range is of great

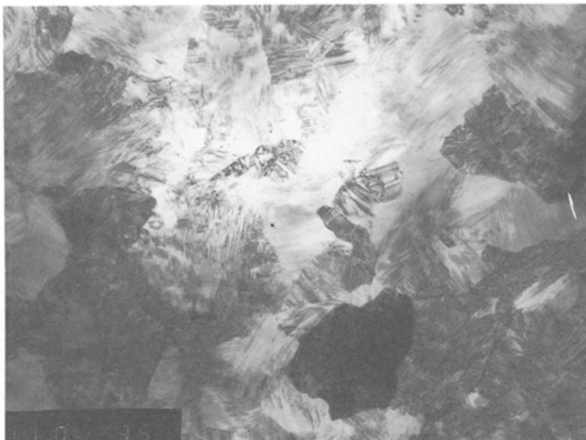

Figure 7 Bright field TEM micrograph for a film deposited at 630 °C and 24 Pa.

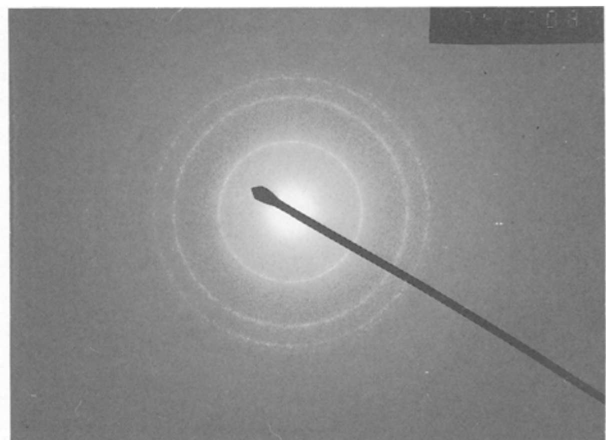

Figure 9 Electron diffraction pattern for a film deposited at 630 °C and 6.66 Pa.

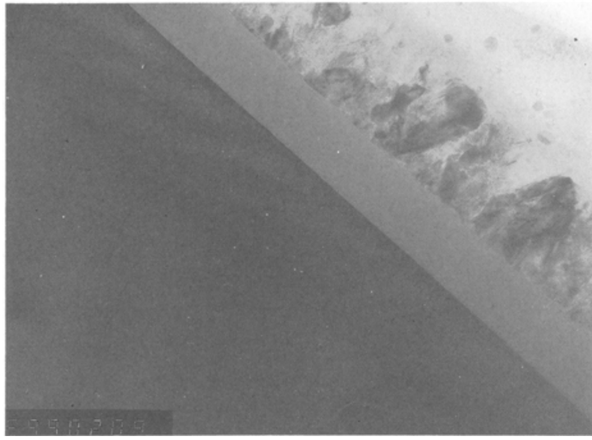

Figure 10 Cross-sectional TEM micrograph for a film deposited at 630 °C and 6.66 Pa.

Figure 12 Electron diffraction pattern for a film deposited at 630 °C and 0.33 Pa.

interest. Moreover [8, 16] the process is extremely cost-effective as a near-standard LPCVD reactor operating at low gas flow rate can be used to grow such films.

3.2.3. Very low pressures (0.03–1.3 Pa)

At very low pressures below 1.3 Pa, an entirely new mode of growth is found. Depositions at temperatures as low as 560 °C have been performed to investigate this new observation more fully as it is of great importance to the manufacture of polycrystalline TFT's on glass substrates. These results also pertain to low temperature epitaxy now being investigated in this pressure range. Fig. 11 is a cross-sectional TEM of a sample grown at 0.33 Pa at 630 °C, the presence of large tooth-shaped single crystals is seen. At the SiO_2 interface only relatively small crystals are present although these are larger than the corresponding crystallites in films at higher pressures, for example in Fig. 10.

The diffraction pattern shown in Fig. 12 was taken sideways through one of the large grains, and shows that the grain is a single crystal with a low density of defects. It reveals the direction of growth to be ⟨0 0 1⟩ normal to the substrates. Conventional TEM examination shown in Fig. 13, confirms the large grain size, the fringes being due to the curved surface of the grains. Electron diffraction patterns through the films using the largest aperture (5 micrometres) show the ⟨1 1 1⟩ ring to be very faint with the strong ⟨0 0 1⟩ orientation, Fig. 14. The trend of these results has been

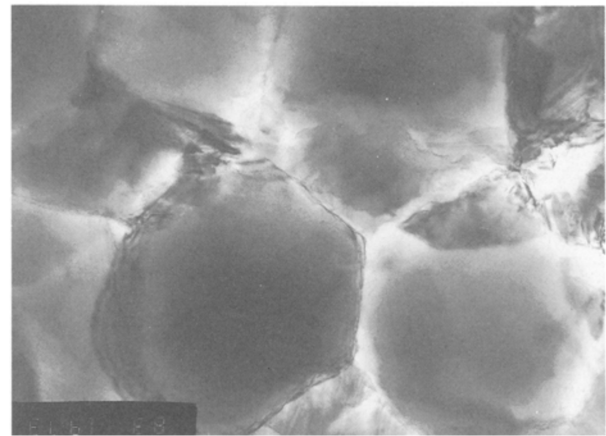

Figure 13 Conventional TEM for a film deposited at 630 °C and 0.33 Pa.

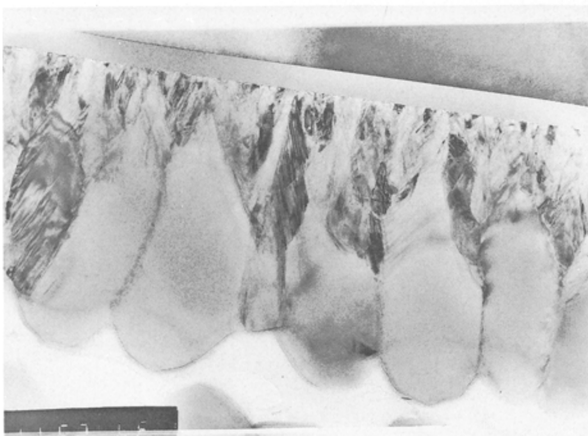

Figure 11 Cross-sectional TEM micrograph for a film deposited at 630 °C and 0.33 Pa.

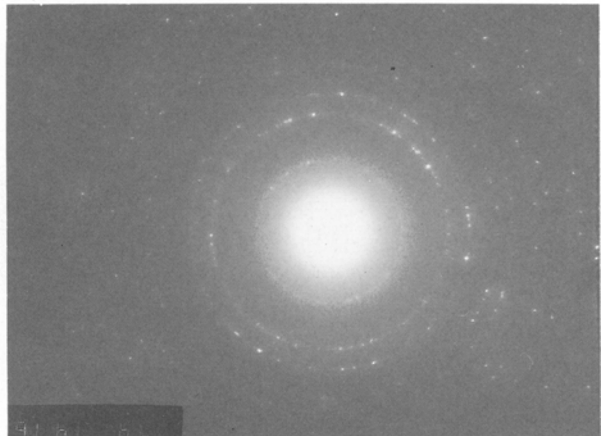

Figure 14 Perpendicular electron diffraction pattern for a film deposited at 630 °C and 0.33 Pa.

Figure 15 Cross-sectional TEM micrographs for films deposited at 590 °C and 0.33 Pa.

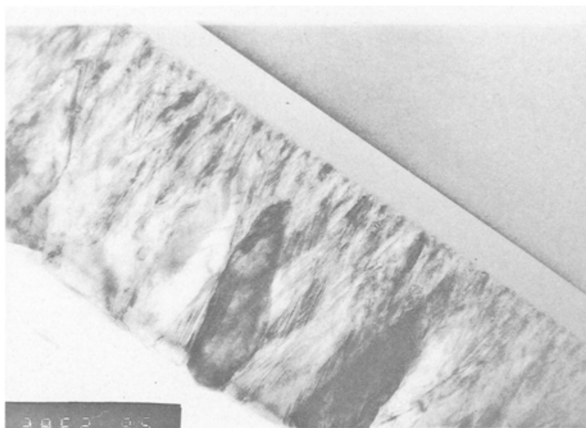

Figure 16 Cross-sectional TEM micrographs for films deposited at 590 °C and 1.33 Pa.

confirmed by Loisel and Joubert [15] using X-ray diffraction, but with the use of a hydrogen carrier gas which makes direct comparison difficult.

If the pressure is increased to 1.3 Pa, at the same temperature, the structure is maintained but the grain size at comparable points in the film is smaller. The region of very fine crystallites at the bottom of the film is broader so that microcrystallites can sometimes reach the surface. Beyond 1.3 Pa the film structure is that described by the intermediate pressure range material.

The behaviour of the film morphology as the temperature is reduced is markedly similar to the effect of an increase in pressure. Figs 15 and 16 show cross-sectional TEMs of films deposited at 590 °C at 0.33 and 1.3 Pa, respectively. It can be seen that as the temperature is decreased the crystallite size decreases. For example, at 1.3 Pa and 590 °C there are bands of microtwins all over the surface of the film, having grown right through the film from the disordered region at the back. The diffraction pattern in this case shows a strong ⟨1 1 1⟩ ring indicating that the preferred ⟨0 0 1⟩ orientation has been lost, and has reverted to material more characteristic of that grown in the intermediate pressure range at higher temperatures. This behaviour has been investigated by other workers more systematically using hydrogen dilution [15], and the general trends confirmed although the actual morphology results differ. TFT devices made in these films are currently being evaluated.

4. Conclusion

The use of a UHV–CVD reactor has been described giving polycrystalline films of unique structural properties at very low pressures which have an important application in the fabrication of liquid crystal displays using 100% silane at < 1.33 Pa. The effect of reactor parameters on the deposition rate and film structure has been presented and the properties of these films will allow the fabrication of high quality polysilicon TFT's on glass substrates at considerably lower temperatures than hitherto.

References

1. L. W. KENNEDY, D. E. H. SMITH and D. V. McCAUGHAN, *J. Sci. Techn.* **48** (1982) 90.
2. T. I. KAMINS, M. M. MANDURAH and K. C. SARASWAT, *J. Electrochem. Soc.* **125** (1982) 90.
3. G. HARBEKE, L. KRAUSBAUER, E. F. STEIGMEIER and A. E. WIDMER, *RCA Rev.* **44** (1983) 287.
4. R. S. ROSLER, *Solid State Techn.* **20** (1977) 63.
5. S. MOROZUMI, K. OGUSHI, T. MISAWA, R. ARAKI and H. OTISHIMA, in "SID84 Digest 919840", p. 316.
6. Y. OANO, K. KOBUKE, N. MUKAU and K. IDE, *Jpn J. Appl. Phys.* **22** (1983) 493.
7. N. NAGASIMA and N. KUBOTA, *J. Vac. Sci. Techn.* **14** (1977) 54.
8. D. B. MEAKIN, P. A. COXON and P. MIGLIORATO, to be published.
9. B. S. MEYERSON, E. GANIN, D. A. SMITH and T. N. NGUYEN, *J. Electrochem. Soc.* **133** (1986) 1232.
10. C. H. J. Van den BREKEL and L. J. M. BOLLEN, *J. Cryst. Growth* **54** (1981) 310.
11. T. J. DONAHUE and R. REIF, *J. Electrochem. Soc.* **133** (1986) 1691.
12. J. H. PURNELL and R. WALSH, *Proc. Roy. Ser A* **293** (1966) 543.
13. B. S. MEYERSON, *J. Electrochem. Soc.* **131** (1984) 2361.
14. K. F. JENSEN, M. L. HITCHMAN and W. AHMED, in Proceedings of the 5th European Conference on CVD, edited by J. O. Carlsson and J. Lindstrom (University of Upsala, Sweden, 1985) p. 144.
15. B. LOISEL and P. JOUBERT, private communication.
16. D. B. MEAKIN, P. A. COXON, P. MIGLIORATO, J. STOEMENOS and N. A. ECONOMOU, to be published.

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