JOURNAL OF MATERIALS SCIENCE **36** (2001) 207–212

Structural variations in polysilicon, associated with deposition temperature and degree of anneal

A. A. PARR, D. J. GARDINER
School of Applied and Molecular Sciences, University of Northumbria at Newcastle, Ellison Place, Newcastle upon Tyne, NEI 8ST, UK

R. T. CARLINE, D. O. KING, G. M. WILLIAMS
DERA, St Andrews Road, Malvern, Worcestershire, WR14 3PS, UK
E-mail: andrea.parr@unn.ac.uk

Raman microscopy has been used to investigate the structure of as deposited and annealed polysilicon films formed by low-pressure chemical vapour deposition. The films were deposited between 620°C and 570°C, and the effects of various thermal annealing conditions on these samples is reported. Components of the polysilicon Raman bands have been categorised according to their wavenumber position and FWHM values. It has been shown that the degree and nature of change in material structure, is dependent upon: the starting material selected, the anneal temperature, and the anneal time.

1. Introduction

Polysilicon is now extensively used for micro-electronic and micro-mechanical structures and hence has been the subject of many studies [1, 2]. Uses of polysilicon thin films include polycrystalline gates, load resistors, and interconnects, amongst other applications on integrated circuit technology [3]. This work was part of a larger project to determine polysilicon suitability for devices such as accelerometers and gyroscopes and identify which deposition temperature and post deposition anneal processes yield the most favourable structure.

Electrical characteristics that determine polysilicon usefulness for electronic device applications are governed by the volume fraction and quality of both grains and grain boundaries [4]. In order to maximise the grain size, the polysilicon is usually deposited in the amorphous or micro-crystalline phase and is then completely crystallised during a post deposition thermal treatment [1]. This type of process yields 'crystallised' polysilicon as opposed to 'as deposited' polysilicon where the film is deposited directly in the polycrystalline phase [1]. Several studies have indicated that the structural properties of crystallised polysilicon are strongly related to the conditions under which the polysilicon was originally deposited [1], particularly deposition temperature and deposition pressure. Decreasing the pressure or increasing the temperature favours the formation of direct polycrystalline material.

Often polysilicon is deposited on a silicon dioxide film, which constitutes the sacrificial layer [5]. Removal of this oxide can present serious stress effects in the polysilicon film, which then cause mechanical device failures, curling or fracture [5]. The origin of the large tensile and compressive intrinsic stresses is straightforwardly related to the polysilicon microstructure [5]. Maier-Schneider [6] reported that after annealing polysilicon films at temperatures higher than the deposition temperature the compressive stress in the film started to decrease with increasing annealing temperature, relaxing nearly completely after annealing at 1100°C. Heating may however, lead to oxygen diffusion from silica to polysilicon and local crystallisation of oxygen-deficient SiO_2. This results in local volume changes and together with thermal expansion mismatch, gives rise to micro and macro strains, formation of dislocations and material bending [7].

The Raman spectrum of single crystal silicon comprises a single band at $\sim$521 cm^{-1}, arising from the triply degenerate T_{2g} phonon. For polycrystalline silicon the Raman signal is more complex and is determined by the material characteristics. Raman microscopy has been recognised as a valuable method for monitoring changes in microstructure. It has been used, for example, to determine stress profiles [8] and map temperature distribution [9] in silicon electronics structures. In this work Raman microscopy has been used to investigate the structural characteristics of Low Pressure Chemical Vapour Deposition (LPCVD) polysilicon films in relation to deposition temperature and degree of anneal. It is a technique that is fast, non-destructive and sensitive to the presence of low concentrations of defects, with sub-micron resolution.

It has previously been shown that a strong relationship exists between the structural order of the silicon matrix and the deposition temperature [1]. Confirmation of this is provided and further detail of the relationship given in this work.

2. Experimental

Two types of samples were analysed.

TYPE 1: 2 μm of polysilicon deposited on 0.5 μm of wet thermal oxide grown on n-silicon (001).
TYPE 2: 2 μm of polysilicon between 0.5 μm layers of phosphorous doped oxide (∼7% by weight phosphorous/oxide) on n-silicon (001).

Type 2 samples were analysed to demonstrate the effect of an additional surface oxide layer together with phosphorous doping. For each set, polysilicon was deposited by LPCVD at temperatures of 620°C, 610°C, 600°C, 590°C, 580°C and 570°C. The source gas used was 100% silane and the deposition pressure was 300 mTorr (40 Pa).

An argon purged Linkam TH1500 heating stage, was used to anneal 5 mm square portions of representative samples, (chosen from results of as deposited samples). The temperature range 900°C to 1200°C was used with annealing times varying from 10 minutes to 3 hours.

A Raman Microline Focus Spectrometer, (MiFS), was used for analysis, which uses cylindrical optics to produce a line focus of the incident laser beam on the surface of the sample. This allowed Raman spectra from 240 points (along the length of the line), to be recorded concurrently. This approach has the advantage of reducing the heating effect at any individual point on the sample compared to a point focus arrangement. Scattered light was then imaged through a non-astigmatic, triple spectrometer, to form a spectrally dispersed image, on a cooled, two-dimensional, charge coupled device (CCD). Binning (summing) these point spectra produced a spectrum representing the average signal along the length of the line, (in this work a ×40 objective was used, giving a line length of ∼140 μm). Incident light of ∼2 mW at the sample from the 488.0 nm line of a cw argon ion laser was used, allowing surface analysis of up to 0.6 μm in depth [10].

Spectra were recorded at 5 random positions on the surface of each sample and peak centres, area centres, FWHM and asymmetry values were calculated: Peak centre is the shift value of the noise weighted highest intensity point in the band; Area centre is the shift value that has an equal area of the band on either side; FWHM is the full width at the half maximum, the maximum being at the 'peak centre;' Asymmetry is given by the ratio of the half maximum width on the low frequency side of the 'peak centre,' to the half maximum width on the high frequency side of the 'peak centre'. All results were calibrated with single crystal silicon as a standard, using the single triply degenerate Raman active T_{2g} phonon mode fixed at 521.00 cm^{-1}.

3. Results

Raman spectra of the as deposited samples (Fig. 1) clearly fall into three distinct varieties of polysilicon with an intermediate (590°C), as described in Table I. Samples deposited at ≥590°C, exhibit a Raman band with a broad feature, at ∼497 cm^{-1}, overlapping the main peak. In addition, a close examination of the spectra reveals that all deposition temperatures produced a small amount of material which exhibited the characteristic amorphous band readily seen for the 570°C sample (shown in Fig. 1, with 5× actual intensity).

Representative samples selected from results in Table I, for further analysis, were those deposited at 620°C, 580°C and 570°C. Spectra from these were fitted using 'peak fit' software and revealed the existence of various 'categories' of polysilicon, as seen in Fig. 2. These 'categories' are defined in Table II, together with a list of peaks used for fitting polysilicon spectra. Subtle differences between type 1 samples and type 2 samples

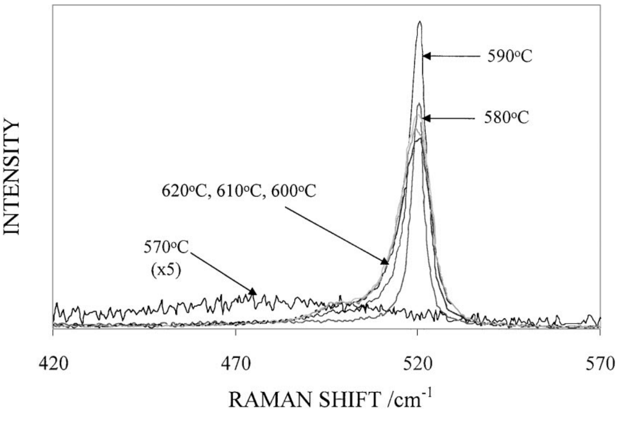

Figure 1 Raman spectra of as deposited polysilicon.

TABLE I Raman data for as deposited polysilicon

Deposition Temperature/°C	Description of Raman Band	FWHM/cm^{-1}	Peak Centre Shift from Single Crystal Silicon/cm^{-1}
620, 610, 600.	The main peak is asymmetrical with a less intense broad band overlapping the base at the lower frequency side.	∼10.0	∼0.8
590	As above but the main peak is less asymmetrical and the broad band at lower frequency is less intense. (Intermediate between 620°C, 610°C, 600°C material and 580°C material.)	∼5.6	∼0.8
580	Almost symmetrical peak with no lower frequency band detected.	∼4.2	∼0.8
570	No detectable polysilicon signal, but band at 475 cm^{-1}, which is characteristic of amorphous silicon.	∼80	∼40.5

TABLE II Peaks used for peak fitting

CATEGORY	RAMAN SHIFT/cm^{-1}	FWHM/cm^{-1}
1		
Peaks with centre and FWHM values close to single crystal silicon, a possible explanation for the small deviations observed being strain variations in the material.	521.00	3.5
	521.00	3.1
	520.90	3.3
	520.70	7.4 (multiple)
	520.65	3.6
	520.20	3.9
	519.80	3.8
2		
Peaks representative of disordered crystalline silicon.	518.70	9.1
	517.40	14.5
3		
Peaks representative of silicon amorphous like in structure.	498.70	15.2

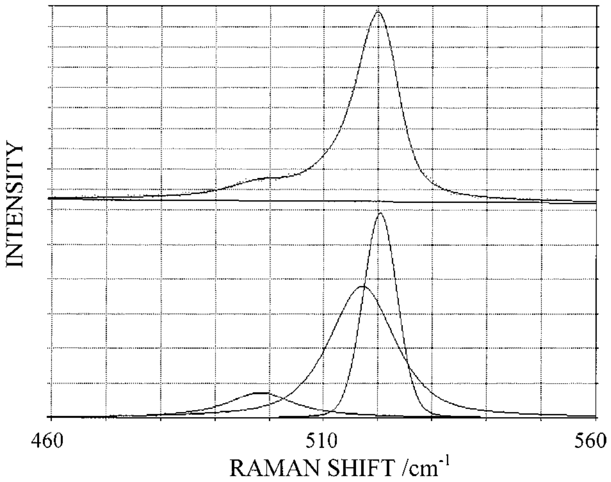

Figure 2 Example of a peak fit result for as deposited 620°C type 1 material.

were detected, together with greatly enhanced signal intensity for type 2 samples compared to type 1.

As deposited 620°C material is composed of category 1, 2 and 3 peaks, where as 580°C material consists of category 1 peaks only and 570°C material contained no detectable polysilicon peak. The percentage area of each Raman band accommodated by a fitted peak of a specific category is plotted in Figs 4 to 7, demonstrating trends associating polysilicon structure with deposition temperature and state of anneal.

The transmission electron microscopy, (TEM), results (Fig. 3) show that only the first 300–400 nm of the polysilicon deposited at 570°C has started to recrystallise (Fig. 3A), with randomly orientated grains, 200–400 nm in size. In the amorphous material above this, smaller crystallites are clearly beginning to form. No crystalline material was detected by Raman microscopy of the surface, due to the low penetration of the incident wavelength employed, in amorphous silicon, (∼1/10 of that in crystalline silicon). Attempts to investigate the composition at the interface with the oxide, using a wavelength of 647.1 nm (from a krypton ion laser) were unsuccessful. After annealing at 1200°C for 1 hour, the 570°C material consists of approximately 930 nm of polysilicon with randomly orientated grains 200–700 nm in size (Fig. 3B). Annealing has caused the amorphous silicon to crystallise and some of the polycrystalline grains are now larger. The orientation, however, was still observed, from diffraction patterns, to be random.

Grain sizes in polysilicon deposited at 580°C (Fig. 3C), range from 100 nm to 700 nm and again, orientation of grains is random. Along the lower interface of the polysilicon layer a large number of relatively small grains can be seen. Annealing at 1200°C for 1 hour, produced material containing grains 200–1000 nm in size, which are tending to be preferentially orientated in the [100] direction, (Fig. 3D), with the structure being more columnar than material deposited at 570°C. The diffraction pattern from this layer also confirmed this preferred orientation. The small crystallites seen along the lower interface in the unannealed sample appear to have grown out.

Polysilicon deposited at 620°C consists of a highly orientated array of very fine grains, inclined at a small angle to the 100 direction of the structure (Fig. 3E). There was no observed change in the structure of the polysilicon following anneal at 1200°C (Fig. 3F), The material appears to be dominated by highly orientated arrays of twins or stacking faults which are probably inclined on (111) planes.

4. Discussion

A possible explanation for the enhanced Raman scattering from type 2 samples, is that the surface oxide layer acts as an anti-reflection coating, directing a greater proportion of the incident light into the sample which may then interact with phonons and produce more scattered light. Downshift and broadening of the silicon phonon band, as seen for polysilicon samples deposited between 620°C and 580°C, (Fig. 1), have frequently been associated with defects [11, 12], particle sizes ($\leq$30 nm) [13, 14], disorder [15] and inhomogeneous strain distribution [16]. More specifically the broad feature which lies to the lower frequency side, seen for polysilicon samples deposited between 620°C and 590°C, (Fig. 1), has been attributed to: surface like modes associated with grain boundaries [17], surface layers of silicon that act as grain boundaries for crystalline inclusions in an SiO_2 matrix [18], the transition layer at the Si-SiO_2 interface [14] and numerous nanometre scale faulted regions revealed by TEM micro-graphs, (believed to result in nanometre scale Si structures, perhaps only a few unit cells in extent) associated with columnar structures [18]. The Raman and TEM results obtained, support association of the 497 cm^{-1} band, with columnar structure as suggested by Tallant [18]. As a single symmetrical peak cannot represent this band, overlap of maxima, as suggested by Verhey [16], is also implied and results are consistent with the theory that red shift and broadening increase with decreasing crystallite size.

At this stage, no post deposition heating had taken place, hence dopant diffusion had not occurred and thermal expansion mismatch at polysilicon/oxide interfaces had had no effect.

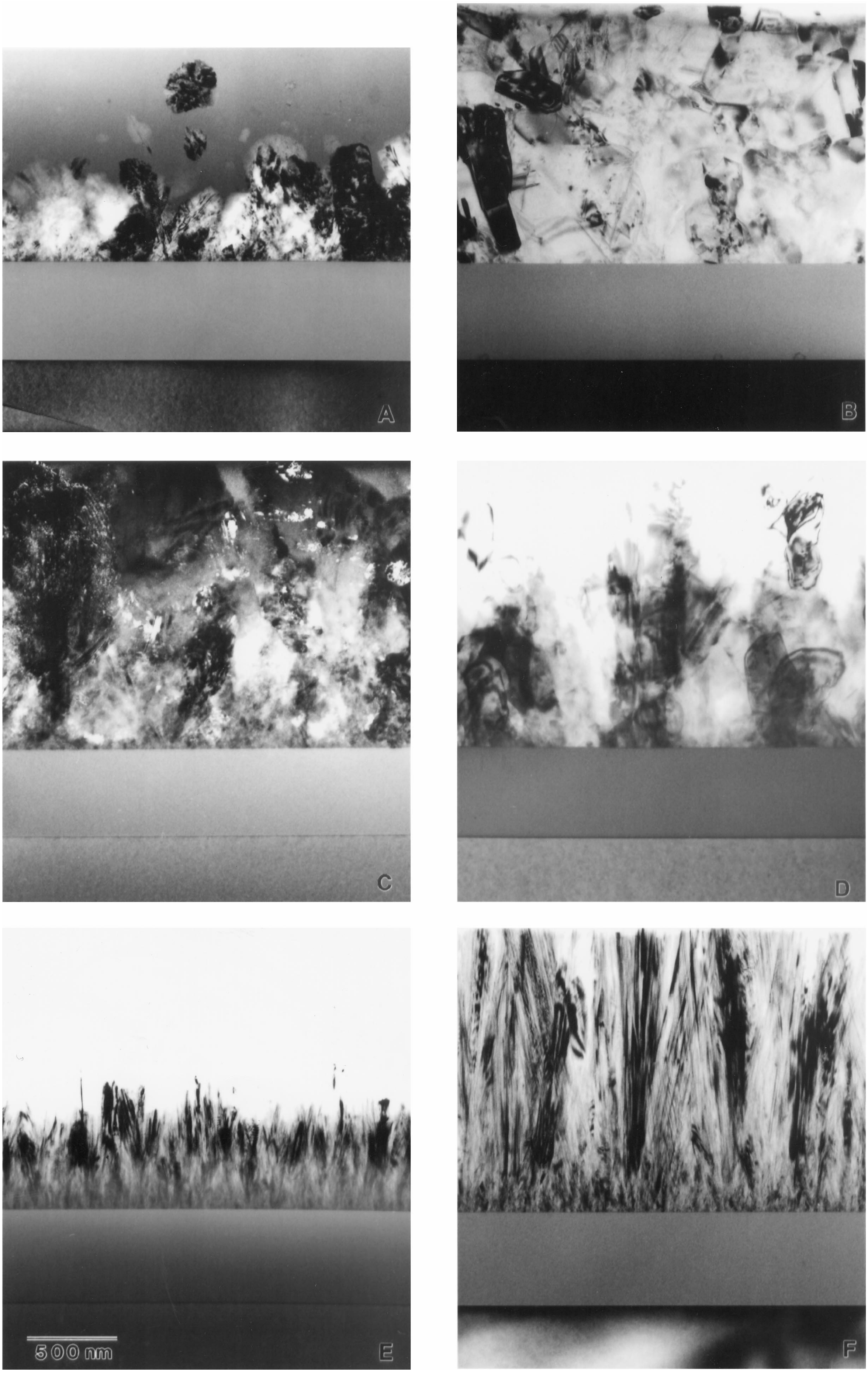

Figure 3 TEM of polysilicon.

4.1. Annealing at constant temperature (900°C), time varying

In type 1 620°C material, the category 3 content remained relatively constant throughout all 900°C anneals, but gradual reduction in category 2 content occurred, accompanied by an increase in category 1 content (Fig. 4). Amorphous silicon in 570°C material, was converted to polycrystalline material by 10 minutes of annealing (Fig. 4), with longer anneal times resulting in reduction in category 2 content and increase in category 1, (as for the 620°C material).

The 580°C material shows finer variations within a category (Fig. 5), identifying a change in material composition after 10 minutes of annealing, which is not seen after 3 hours of annealing. Band FWHM and integrated intensity values provided additional information, on this change, showing an increase in band intensity, (by a factor of 2,) after a 10 minute anneal, together with a small decrease in band width produced by a 3 hour anneal. A possible explanation for these observations is an initial increase in 519.8 cm^{-1} polysilicon, (from realignment) during the first 10 minutes of anneal, followed by removal of tensile stress in this polysilicon with further anneal, to produce more 520.2 cm^{-1} polysilicon. Confirmation of the true cause of these observations has not been possible from these measurements alone, due to the variety of structural considerations concerning Raman peaks.

Type 1 and type 2 samples, which have corresponding deposition temperatures and anneal conditions, produced very similar Raman spectra, both as deposited and when annealed. Type 2 material showed essentially the same trends as type 1 but at different rates. For 620°C material, reduction of category 2 content accompanied by an increase in category 1 content occurred to a lesser extent in type 2 and likewise a 10 minute anneal produced 570°C material consisting of majority category 2 rather than category 1 peaks. 580°C material also showed the same trends in type 2 as in type 1, but at a reduced rate.

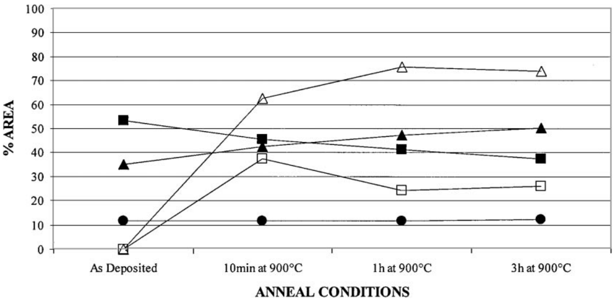

Figure 4 620°C type 1 material, annealed for varying times (● Category 3 ■ Category 2 ▲ Category 1) and 570°C type 1 material, annealed for varying times. (○ Category 3 □ Category 2 △ Category1).

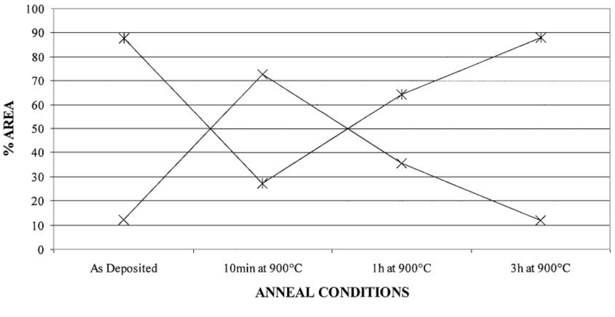

Figure 5 580°C type 1 material, annealed for varying times. (× Centre = 519.8 cm^{-1} FWHM = 3.8 cm^{-1}, Centre = 520.2 cm^{-1} FWHM = 3.9 cm^{-1}, ◇ Centre = 521.0 cm^{-1} FWHM = 3.1 cm^{-1}).

In summary, annealing at 900°C does provide enough energy to restructure some forms of polysilicon, but not category 3. The degree of change is proportional to length of anneal and the sample composition, type 1 showing more extensive changes than type 2.

4.2. Annealing at varying temperatures, time constant (1 hour)

1 hour anneals at elevated temperatures, up to 1200°C, created further changes in structure with all type 1 samples eventually being annealed to category 1 silicon only, and in the case of the 580°C material, a category 1 material closer to single crystal silicon.

Annealing for 1 hour at 1200°C (Fig. 6), removed category 2 and 3 material from 620°C and category 2 from 570°C type 1 samples, with the 1050°C anneal indicating that removal of the category 3 peak from 620°C material, proceeded via conversion to category 2 peaks.

Annealing at 1050°C also produced a key change in the type 1 580°C single category material (Fig. 7), introducing the 521.0 cm^{-1} peak and removing the 519.8 cm^{-1} peak. Increases in temperature beyond 1050°C increased the proportion of the 521.0 cm^{-1} peak.

Complete removal of category 2 peaks from type 2 620°C material, did not occur. In addition a category 1

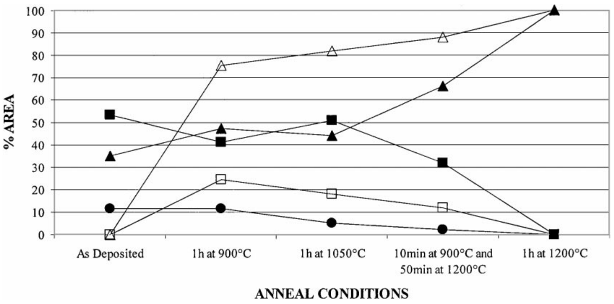

Figure 6 620°C type 1 material, annealed at varying temperatures (● Category 3 ■ Category 2 ▲ Category 1) and 570°C type 1 material, annealed at varying temperatures. (○ Category 3 □ Category 2 △ Category 1).

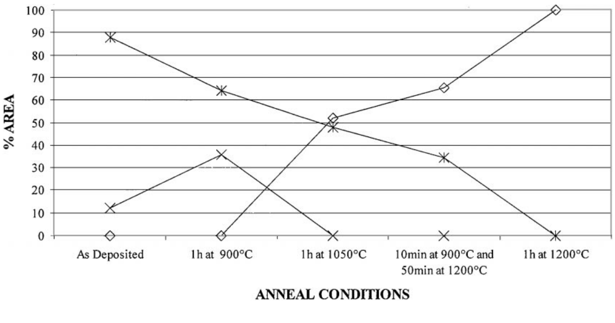

Figure 7 580°C type 1 material, annealed at varying temperatures. (× Centre = 519.8 cm^{-1} FWHM = 3.8 cm^{-1}, Centre = 520.2 cm^{-1} FWHM = 3.9 cm^{-1}, ◇ Centre = 521.0 cm^{-1} FWHM = 3.1 cm^{-1}).

peak was detected in type 2 material, which was broader and at lower frequency than the equivalent peak in type 1 material. Type 2 570°C material responded much the same as type 1 to high temperature anneals, however, individual peak analysis showed that after annealing at 1200°C, type 1 material resembled single crystal silicon more closely than type 2. Type 2 580°C material also followed the same trends observed in type 1, but with less extensive changes at each temperature.

To summarise, annealing at 1200°C for 1 hour converted all samples to similar crystalline materials, with no amorphous or lower frequency bands detected and Raman spectra closely resembling that of single crystal silicon. The exact composition of the material produced depended upon the deposition temperature of the polysilicon, degree of anneal and the presence of doped oxide either side of the polysilicon.

Phosphorus doping, as in annealed type 2 polysilicon, has been reported to enhance the recrystallization process, producing a higher grain size in the doped regions [8]. This affects internal stress levels, (possibly governed by surface diffusion of adatoms,) and low deposition temperature samples are thought to require a higher anneal temperature, to produce zero stress, than those deposited at higher temperatures. Our results indicate an improved recrystallization rate for samples doped with phosphorus via surrounding oxide, however, this is coupled with restricted re-growth yielding an end product more distorted from single crystal silicon.

5. Conclusion

The surface layer (∼0.6 μm) of the samples supplied ranges from amorphous silicon (deposited at 570°C), through well-ordered polysilicon (deposited at 580°C) to polysilicon, consisting of category 1, 2 and 3 silicon, (deposited at 600°C, 610°C or 620°C).

Annealing reduced levels of amorphous, category 3 and category 2 silicon contained in each of the samples, to produce well ordered crystalline material. The degree of change in material structure, is dependent upon: the starting material selected, the anneal temperature, and the anneal time. Temperatures as low as 900°C have been shown to produce structural changes in microcrystalline samples with temperatures of 1050°C and above producing a second level of change. The level of change in material sandwiched between doped oxide layers has been shown to be more restricted than that for material with no dopant and no surface oxide layer.

Further studies are now in progress to identify the effect of external stress on polysilicon, which can then be collated with results presented above, to provide a database, to which faulted polysilicon structures can be compared.

Acknowledgement

The authors thank DERA for financial support.

References

1. A. T. VOUTSAS, M. K. HATALIS, J. BOYCE and A. CHIANG, *J. Appl. Phys.* **78**(12) (1995) 6999.
2. M. FURTSCH, M. OFFENBERG, A. VILA, A. CORNET and J. R. MORANTE, *Thin Solid Films* **296** (1997) 177.
3. R. BISARO, J. MAGARIÑO, N. PROUST and K. ZELLAMA, *J. Appl. Phys.* **59**(4) (1986) 1167.
4. W. CZUBATYJ, D. BEGLAU, B. S. CHAO, J. GONZALEZ-HERNANDEZ, D. A. PAWLIK, P. KLERSY, D. JABLONSKI and R. HIMMLER, *J. Vac. Sci. Technol.* **A9**(2) (1991) 294.
5. M. S. BENRAKKAD, M. A. BENITEZ, J. ESTEVE, J. M. LÓPEZ-VILLEGAS, J. SAMITIER and J. R. MORANTE, *J. Micromech. Microeng.* **5** (1995) 132.
6. D. MAIER-SCHNEIDER, J. MAIBACH, E. OBERMEIER and D. SCHNEIDER, *ibid.* **5** (1995) 121.
7. S. S. GORELIK, T. B. SAGALOVA and YU. S. SAFONOV, *Inorganic Materials* **32**(4) (1996) 351.
8. J. R. MORANTE, J. SAMITIER and M. S. BENRAKKAD, *Microelectronics Journal* **28**(4) (1997) 433.
9. M. BOWDEN, D. J. GARDINER, A. A. PARR, R. T. CARLINE, R. J. BOZEAT, R. J. T. BUNYAN and M. WARD, Microsc. Semicond. Mater. Conf., Inst. Phys. Conf. Ser. Vol. 157 (1997).
10. I. DE WOLF, *Semicond. Sci. Technol.* **11** (1996) 139.
11. K. MIZOGUCHI, Y. YAMAUCHI, H. HARIMA, S. NAKASHIMA, T. IPPOSHI and Y. INOUE, *J. Appl. Phys.* **78**(5) (1995) 3357.
12. G. HARBEKE, L. KRAUSBAUER, E. F. STEIGMEIER, A. E. WIDMER, H. F. KAPPERT and G. NEUGEBAUER, *Appl. Phys. Lett.* **42**(3) (1983) 249.
13. I. H. CAMPBELL and P. M. FAUCHET, *Solid State Communications* **58**(10) (1986) 739.
14. S. R. GOODES, T. E. JENKINS, M. I. J. BEALE, J. D. BENJAMIN and C. PICKERING, *Semicond. Sci. Technol.* **3** (1988) 483.
15. M. S. BENRAKKAD, A. PEREZ-RODRIGUEZ, T. JAHWARI, J. SAMITIER, J. M. LOPEZ-VILLEGAS and J. R. MORANTE, *Mat. Res. Soc. Symp. Proc.* **343** (1994).
16. J. VERHEY, U. BISMAYER, B. GÜTTLER and H. LUNDT, *Semicond. Sci. Technol.* **9** (1994) 404.
17. Z. IQBAL and S. VEPREK, SPIE Vol. 794 (1987) p. 179.
18. D. R. TALLANT, T. J. HEADLEY, J. W. MEDERNACH and F. GEYLING, *Mat. Res. Soc. Symp. Proc.* **324** (1994) 255.

Received 23 June 1999
and accepted 2 June 2000