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Ultralow-Stress Silicon-Rich Nitride Films for Microstructure Fabrication

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We have set up a low-pressure chemical vapor deposition (LPCVD) system enabling us to deposit ultralow stress (≤10 Mpa), single layer silicon-rich nitride films at high temperatures (≤900°C) with fast deposition rates for the fabrication of microstructures. Silicon-rich nitride films deposited at high temperatures have ultralow stress and are relatively independent of silicon- and nitrogen-containing gas flow ratios during deposition. Deposition process parameters were optimized employing the Taguchi method, and no post-deposition process was required to obtain low-stress films. Detailed study of the effects of deposition parameters on film properties is also presented. The high temperature deposited ultralow-stress silicon-rich nitride film is resistant to all commonly used silicon anisotropic etchants (KOH, EDP, TMAH, hydrazine) and is an ideal material for the fabrication of various microstructures.

1. Introduction

One of the key technologies in micro electromechanical system (MEMS) fabrication is the ability to prepare low-stress films for the fabrication of various microstructures. Popular micro-structures such as cantilever beams, microbridges, micromirrors, and membranes all require deposited low stress films to avoid bending, buckling or breaking after these structures are released by surface or bulk micromachining processes. Thin films commonly used in IC fabrication such as thermal oxide or low-pressure chemical vapor deposition (LPCVD) stoichiometric nitride (Si_3N_4), although they have excellent electrical properties, are either mechanically too weak or have too large a residual stress which renders these films useless for micro-structures. Techniques to reduce stress using oxide/nitride/oxide multilayers (tensile and compressive stress compensation) or variations in film composition (SiN_x) by sputtering/PECVD have been proposed; LPCVD silicon-rich nitride seems to be the most attractive material because of its process simplicity, IC compatibility, and controllable mechanical/optical/thermal properties.(1–5)

As shown by Sekimoto *et al.*,(1) in LPCVD, the preparation of a silicon-rich nitride film was investigated as a function of deposition temperature and reactant gas ratio (DCS SiH_2Cl_2/NH_3). Residual stress in the deposited nitride film decreases sharply with increasing reactant gas ratio, and even reverses from tension to compression at a high reactant gas ratio. However, we observed in our experiments that deposition at a high reactant gas ratio has some drawbacks. First, properties of the nitride film are very sensitive to the reactant gas flow ratio, and the process window is too narrow to control. Only small changes in the DCS/NH_3 ratio lead to relatively large variation in film properties such as refractive index and mechanical stress. Second, high reactant gas ratios also resulted in large nonuniformity in the film thickness and refractive index, which is undesirable in microfabrication. Thermal oxidation on LPCVD silicon-rich nitride film to reduce the film's residual stress was proposed by Chou et. al.(6) Due to stress compensation on the nitride by the growth of the top oxide, an ultralow residue stress film (10 Mpa) could be achieved. However, this method requires a long, high temperature process (1,100°C, 3 h) and is limited to a certain range of nitride thickness, as the oxidation of nitride films is a self-limited process.

We have set up a LPCVD system enabling us to deposit ultralow-stress (≤10 Mpa), single layer silicon-rich nitride films at high temperatures (≤900°C) with fast deposition rates for the fabrication of micro-structures. Process parameters for deposition were optimized using the Taguchi method without any post-deposition process. Detailed study of the effects of deposition parameters on the film properties is also presented.

2. Experiment

With the Taguchi methodology, which is based on statistical factorial experimental design, even for many experiment variables, only a relatively small number of experiments need to be performed, and the effects of individual process variables on film properties are clearly seen. The Taguchi method was employed to optimize the film deposition process. Although there were many process parameters to vary in LPCVD, we focused on only three important variables: deposition temperature (T), SiH_2Cl_2/NH_3 reactant gas ratio (R), and deposition pressure (P).

Four-inch p-type silicon (100) wafers were used as substrates. After a standard cleaning procedure, nitride films were deposited under various conditions designed by the Taguchi method as summarized in Table 1. The thickness and refractive index of the nitride films, as well as their uniformity across the wafers, were measured by an ellipsometer and a Nanospec. The residual stress of nitride films was determined by measuring the change in wafer curvature using a commercial stress measurement system (Tencor FLX-2320). Chemical compositions of the nitride films were analyzed quantitatively by X-ray photoelectron spectroscopy (XPS), and Fourier-Transform infrared spectroscopy (FTIR).

Table 1.
Levels for deposition parameters.

Factors	Levels		
	A	B	C
Deposition pressure (m Torr)	120	250	350
Reactant gas ratio (sccm/sccm)	2	5	9
Deposition temperature (°C)	800	850	900

Two types of post-thermal processes (rapid thermal annealing (RTA), and furnace annealing) were performed on high temperature deposited silicon-rich nitride films (900°C, SiH_2Cl_2:NH_3 ratio 5, 120 mTorr, 0.4 μm, 2.2 MPa) to study the annealing effect. Finally, various microstructures were fabricated by either back etching (BE) or front etching (FE) using commonly used silicon anisotropic etchants.

3. Results and Discussion

3.1 *Film stress and refractive index*

In general, the residual stress in CVD films is a complicated combined result of many factors,(7,8,9) depending on the fabrication process, and is well known to vary with the film thickness. Residual stress is caused partially by thermal effects, the mismatch of thermal expansion coefficients between the deposited film and substrate. For films deposited by CVD methods, the actual stress measured often differs considerably from that caused solely by the thermal stress, and the difference is attributed to so-called intrinsic stress which strongly depends on process parameters. For the large intrinsic stress in stoichiometric silicon nitride, a possible explanation is proposed by Noskov *et al.*(8) that Si-H and N-H bonds dissociate and rearrange to create stable Si-N bonds resulting in film shrinkage during and after deposition, therefore increasing the tensile stress. The hydrogen content is highly related to process parameters such as deposition temperature, reactant gas composition, and post-processing such as ion bombardment and annealing.

As shown in Table 2, the Taguchi method reveals that the process parameters which affect the residual stress in LPCVD silicon-rich nitride are, in decreasing importance, *R*, *T*, and *P*. Residual stress decreases at higher reactant gas ratios (*R*) and higher deposition temperatures (*T*). The reactant gas ratio strongly affects the chemical composition of deposited films, resulting in noticeable changes in the refractive index, residual stress and etching rate. Temperature was reported to be an effective factor in the preparation of low-stress silicon-rich nitride film.(1) However, there is no report regarding high temperature (>850°C) deposited LPCVD silicon-rich nitride.(1–5) Much of the earlier work was done by keeping temperatures below 850°C and using reactant gas ratios as an optimization variable. This is effective, but the film contained serious nonuniformities and was not easily controlled in the deposition process. We have designed and set up a LPCVD system enabling us to deposit ultralow-stress (≤10 Mpa), single layer silicon-rich nitride films at

Table 2.
a) Details of deposition conditions designed by the Taguchi method.

Wafer ID	*T*	*R*	*P*	Index	Stress (Mpa)
SiN1	A	A	A	2.086	1189
SiN2	A	B	B	2.174	561.3
SiN3	A	C	C	2.33	77
SiN4	B	A	B	2.03	712.5
SiN5	B	B	C	2.3	19.1
SiN6	B	C	A	2.63	–214.5
SiN7	C	A	C	2.066	46.4
SiN8	C	B	A	2.37	2.2
SiN9	C	C	B	2.8	–180.6

b) Influence of process parameters on residual stress.

Process parameters	Average SN ratio η		
	A	B	C
Deposition temperature (*T*)	0.768	–8.932	–8.74
Reactant gas ratio (*R*)	1.072	–4.284	–3.537
Deposition pressure (*P*)	–7.312	–2.357	4.3

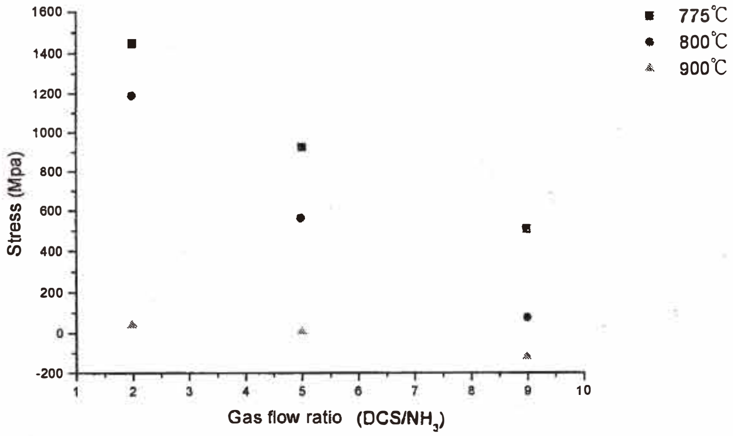

Fig. 1(a). Film stress as a function of gas flow ratio for various deposition temperatures at deposition pressure 140 mTorr.

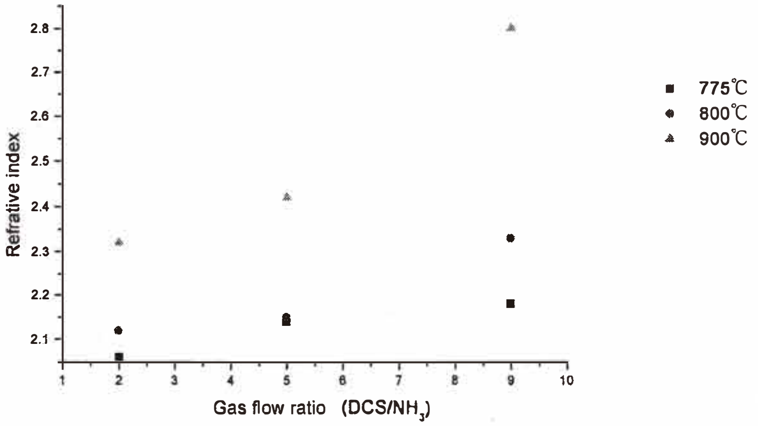

Fig. 1(b). Film refractive index as a function of gas flow ratio for various deposition temperatures at deposition pressure 140 mTorr.

high temperatures (≤900°C) with fast deposition rates. We found that silicon-rich nitride films deposited at high temperatures have ultralow stress and are relatively independent of the gas flow ratio.

Figure 1(a) shows film stress as a function of gas flow ratio for various deposition temperatures; Fig. 1(b) shows the corresponding refractive index. The refractive index increases with higher gas flow ratio (*R*) and higher deposition temperature. Physically, the refractive index is determined by the chemical composition (Si/N ratio) and the atomic density.(4) The refractive index increases with the Si/N ratio, due to the higher polarization of silicon compared to nitrogen. The refractive index of stoichiometric nitride is 2, while that of silicon is 3.6.

3.2 *Material characterization*

As shown in Fig. 2, material properties of high temperature deposited silicon-rich nitride were characterized by a variety of techniques. The microstructure of the film was analyzed by X-ray diffraction (XRD), but no diffraction peaks except those corresponding to the substrate were found. The study revealed that the film is amorphous. The chemical composition of the deposited film was analyzed quantitatively by XPS and FTIR. The binding-energy spectrum as well as the relative atomic composition of the film was determined by XPS and is depicted in Fig. 2(d). The silicon to nitrogen ratio increases with the reactant gas ratio. FTIR measurements were used to determine the hydrogen content in the film; however, in our experiment, except in the stoichiometric nitride (Si_3N_4) deposited at 775°C, no absorption peaks were found for Si-H and N-H. The amount of hydrogen in high temperature deposited silicon-rich nitride films is lower than the measurement limit by FTIR.

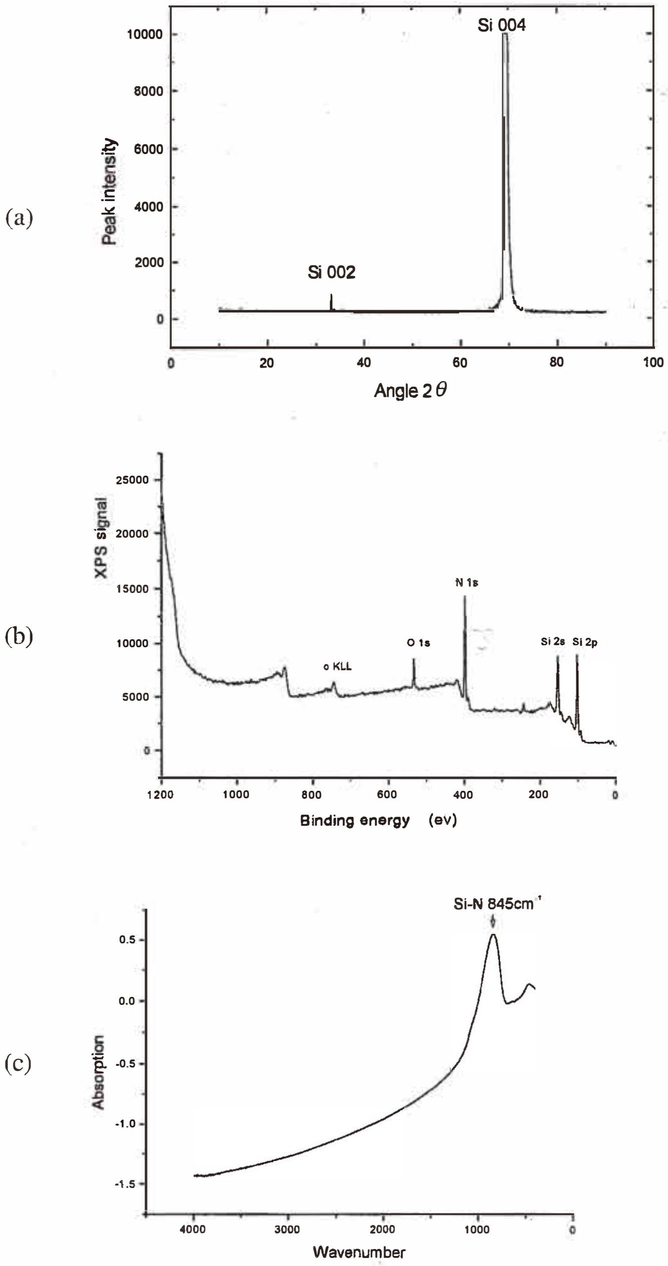

Fig. 2. Characterization of silicon-rich nitride film deposited at 900°C with gas flow ratio of 2. (a) XRD measurement, (b) XPS measurement, (c) FTIR measurement.

(d)

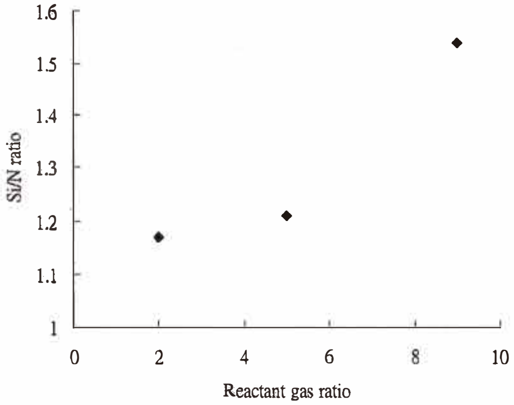

Fig. 2 (continued). (d) Si/N ratio as a function of gas flow ratio deposited at 900°C and 140 mTorr.

3.3 *Post-deposition annealing*

Two types of post-deposition annealing processes (RTA and furnace annealing) were performed on high temperature deposited silicon-rich nitride to observe the stress change caused by the annealing process. For RTA, the samples were annealed in a commercial AG system at temperatures between 900°C and 1100°C for 3 min. For furnace annealing, the samples were annealed in a standard oxidation furnace at temperatures between 900°C and 1,100°C for 30 min. In both cases, the annealing was carried out in nitrogen ambient. Details of the thermal cycle are summarized in Table 3. We found that not only does residual stress increase if the annealing temperature is higher than the deposition temperature, but also that it is quite sensitive to the annealing temperature but not to the annealing time. Since the annealed samples are still amorphous as revealed by XRD, the increased stress is caused by shrinkage of the film and not changes in film microstructure.

Table 3.
RTA and furnace annealing of silicon-rich nitride (initial stress 2.2 MPa).

	Annealing temperature (°C)	Annealing time (min)	Stress (Mpa)
Sample 1	900	3	12.4
Sample 2	900	30	8.6
Sample 3	1,100	3	124
Sample 4	1,100	30	144

3.4 *Model for high temperature deposited films*

Based on the above observations, we propose a new mechanism to explain ultralow stress of the high temperature deposited nitride film: higher temperature (T) modifies the chemical reaction processes, resulting in not only reduction of intermediate products containing hydrogen, such as SiNH*, but also in little shrinkage of the film during and after deposition. Both the desorption rate of intermediate products and the mobility of adsorbed reactants increase with higher process temperatures in LPCVD.(7)

Uniformity of deposited film is an important issue in microfabrication and is dictated by mass transport effects, a larger supply of reacting species at the edge than in the center of the wafer leading to a higher deposition rate at the edge.(4) Mass transport effects dominate, especially when the larger gas flow ratio (R), the higher deposition pressure (P), and the higher deposition temperature (T) all lead to a smaller diffusion length of reacting species and an undesirable nonuniformity. We found in our experiment that ultralow-stress nitride film deposited at higher T (900°C)/lower R (2) is more uniform than that at lower T (850°C)/higher R (6) since R has a significant effect on nonuniformity as observed in the study carried out with the Taguchi method.

3.5 *Etching of deposited films*

The etching rate was qualitatively studied using phosphoric acid (H_3PO_4, 85%,175°C), buffer oxide etchant (BOE), and reactive ion etching (RIE, RF power 150 W, frequency 13.56 MHz, gas flow SF_6/Ar 50 sccm/5 sccm, pressure 80 mTorr). Phosphoric acid and RIE etching were commonly used for patterning the nitride film. In surface micromachining, the nitride may be exposed to an HF-based etchant for a long time. We found that in phosphoric and BOE, the etching rate of a silicon-rich nitride film, which was denser than stoichiometric nitride, is reduced. In our case, silicon-rich nitride remains the same after dipping in BOE for one day. However, a faster etching rate of silicon-rich nitride film using RIE is observed. In RIE, fluorine is the active component to remove silicon; in silicon-rich nitride, the higher the content of silicon, the higher the etching rate.

Ultralow-stress silicon-rich nitride film is resistant to all commonly used silicon anisotropic etchants (KOH, EDP, TMAH, hydrazine) and is an ideal material for the fabrication of various micro-structures. After a long period of high temperature anisotropic etching, the film has no pinholes, suitable for etching stop. Figures 3(a), 3(b) and 3(c) show the scanning electron micrographs of micromachined cantilever beams, microbridges, and coils to demonstrate the excellent qualities of silicon-rich nitride. There is no noticeable deformation, indicating that the residual stress has been reduced in the high temperature deposition process.(10) Figure 3(d) shows the microstructure as a mechanical support for thermal sensing and heating devices. Ultralow stress, dielectric properties (low thermal conductivity) and IC compatibility make silicon-rich nitride very attractive for microsensor applications. Figure 3(e) shows a photograph of a large flat torsion mirror with an area 500 μm × 500 μm with two 150 μm × 15 μm supporting beams. The robust mechanical properties of silicon-rich nitride make it suitable for versatile mechanical structures. Figure 3(f) is a photograph of a flat and highly optical transparent circular membrane 6 cm in diameter. It is a suitable material for an X-ray mask.(1)

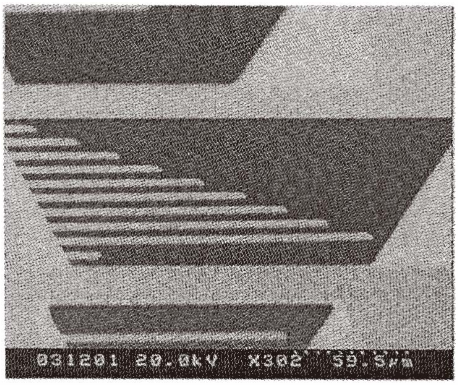

Fig. 3(a). Micromachined cantilever beams.

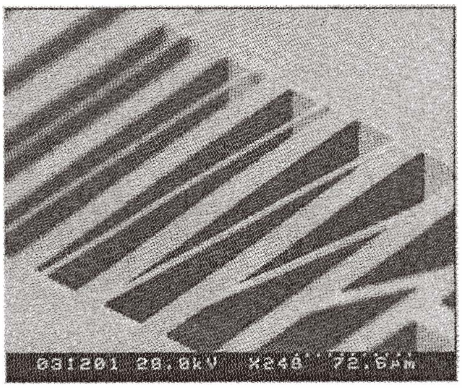

Fig. 3(b). Micromachined microbridges.

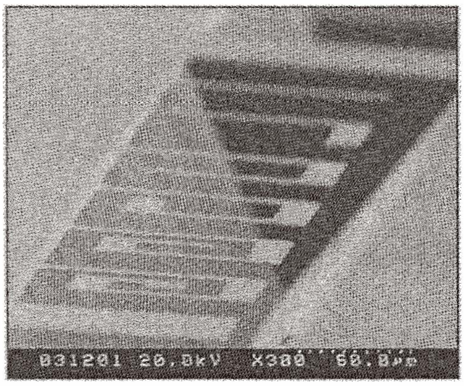

Fig. 3(c). Micromachined cantilever coils.

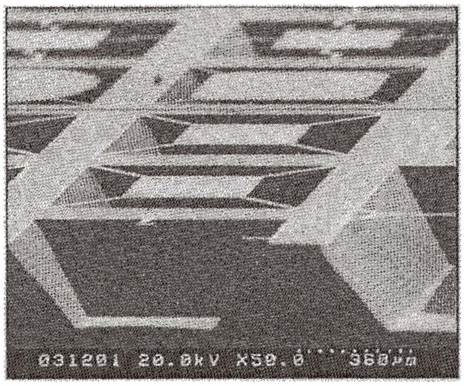

Fig. 3(d). Micromachined floating plates.

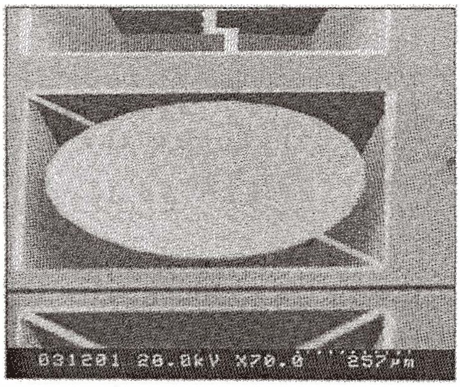

Fig. 3(e). Micromachined circular mirror 500 μm in diamater and two 150 μm × 15 μm supporting beams.

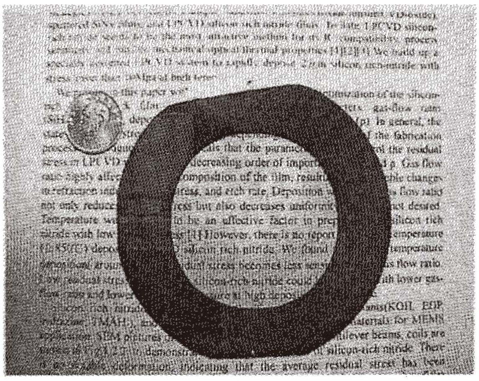

Fig. 3(f). Micromachined circular membrane 6 cm in diameter.

4. Conclusion

We have set up a LPCVD system enabling us to deposit ultralow-stress (≤10 Mpa) single layer silicon-rich nitride films at high temperatures (≤900°C) with fast deposition rates for the fabrication of microstructure. The silicon-rich nitride films deposited at high temperatures have ultralow stress and are relatively independent of the reaction gas flow ratio. The process parameters for deposition were optimized using the Taguchi method. Without any post-deposition processing, low-stress films can be routinely obtained. These high temperature deposited ultralow-stress silicon-rich nitride films are resistant to all commonly used silicon anisotropic etchants (KOH, EDP, TMAH, hydrazine) and are ideal materials for the fabrication of various micro-structures utilizing surface or bulk micromachining etching techniques.

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References

1 M. Sekimoto, H. Yoshihara and T. Ohkubo: J. Vac. Sci. Technol. **4** (1982) 1017
2 C. H. Mastraangelo, Y. C. Tai and R. S. Muller: Sensors and Actuators A **21–23** (1990) 856
3 R. A. Stewart, J. Kim, E. S. Kim, R. M. White and R. S. Muller: Sens. Materials **2** (1991) 285
4 J. G. E. Gardeniers, H. A. C. Timans and C. C. G. Visser: J. Vac. Sci. Technol. A **5** (1996) 2879
5 P. J. French, P. M. Sarro, R. Malee, E. J. M. Fakkeldij and R. F. Wolffenbuttel: Sensors and Actuators A **58** (1997) 149
6 B. C. S. Chou, J. S. Shie and C. N. Chen: IEEE Electron Device Letters **12** (1997) 599
7 M. Stadtmueller: J. Electrochem. Soc. **12** (1992) 3669
8 A. G. Noskov, E. B. Gorokhov, G. A. Sokolova, E. M. Trukhanov and S. I. Stenin: Thin Solid Films **62** (1988) 800
9 D. Maier-Schneider, A. Ersoy, J. Maibach, D. Schneider and E. Obermeier: Sens. Materials **7** (1995) 121
10 W. Fang and J. A. Wickert: J. Micromech. Microeng. **6** (1996) 301