J. of the Korean Sensors Society
Vol. 14, No. 5 (2005) pp. 357 - 361

Fabrication of low-stress silicon nitride film for application to biochemical sensor array

Young-Soo Sohn†

Abstract

Low-stress silicon nitride (LSN) thin films with embedded metal line have been developed as free standing structures to keep microspheres in proper locations and localized heat source for application to a chip-based sensor array for the simultaneous and near-real-time detection of multiple analytes in solution. The LSN film has been utilized as a structural material as well as a hard mask layer for wet anisotropic etching of silicon. The LSN was deposited by LPCVD (Low Pressure Chemical Vapor Deposition) process by varing the ratio of source gas flows. The residual stress of the LSN film was measured by laser curvature method. The residual stress of the LSN film is 6 times lower than that of the stoichiometric silicon nitride film. The test results showed that not only the LSN film but also the stack of LSN layers with embedded metal line could stand without notable deflection.

Key Words : sensor array, low stress silicon nitride, micromachine, microsphere, electronic tongue

1. Introduction

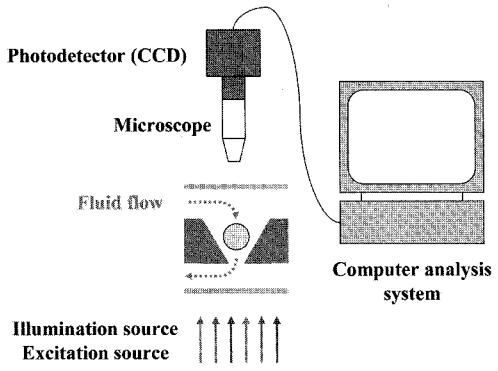
In microsensor applications, thin films are widely used as the supporting and isolating materials such as membrane and bridge structure. The properties of these thin films are critical to the performance of the sensors[1-3]. Among the thin films, silicon nitride films has been widely used in microelectronics technology as an insulator, a material protecting parts of silicon from thermal oxidation in LOCOS (Local Oxidation of Silicon) process for the isolation between transistors, and a mask layer for wet anisotropic etching of silicon. Although silicon nitride films can be deposited by low pressure chemical vapor deposition (LPCVD), plasma enhanced chemical vapor deposition (PECVD) and atmospheric pressure chemical vapor deposition (APCVD) the work presented here utilizes an LPCVD system[4,5].

A chip-based multianalyte sensor array composed of chemically derivatized polymeric microspheres selectively arranged in micromachined cavities localized on the silicon wafer has been developed at the University of Texas at Austin, which is called the "electronic tongue". The name comes from the fact that it mimics many of the features exhibited by the human sense of taste such as pattern recognition. Sensing occurs via colorimetric and fluorescence changes to receptors or/and indicator molecules that are covalently attached to termination sites on the polymeric microspheres. The trans-wafer openings of the micromachined cavities allows for both fluid (beverages, biological samples) flow through the microchambers for reaction/analysis and optical access to the chemically sensitive microspheres. Data streams are acquired for each of the individual microspheres using a photodetector, typically charge-coupled device (CCD). The resulting patterns can be analyzed using a computer for simultaneous and near-real time analyte identification and quantification[6-8]. Fig. 1 shows schematic representation of the "electronic tongue" system. An optical source is positioned above or below the micromachined cavities. Then the light signals which have passed through the microspheres are acquired by the CCD located opposite to the light source. A number of important experiments to demonstrate the feasibility and utility of the array system have already been completed. Table 1 summarizes the analytes that have been successfully detected in our current micromachined platform[9].

In the present study a LSN (low stress silicon nitride) film was deposited to have desirable physical charac-

Deagu Gyeongbuk Institute of Science & Technology : 26th Floor, Samsung Financial Plaza : 110 Ducksan-Dong, Jung-Gu, Daegu

†Corresponding author: sohnys@dgist.ac.kr
(Received : May 24, 2005, Accepted : August 2, 2005)



(a)

(b)

Fig. 1. Schematic representation of the "electronic tongue" system; (a) A light source irradiates an array of microspheres in the micromachined cavities for optical detection. The passed light is analyzed by a photodetector, typically a CCD and (b) The apparatus for electronic tongue system such as CCD, microscope and the specific pattern of the sensor array on the monitors are shown.

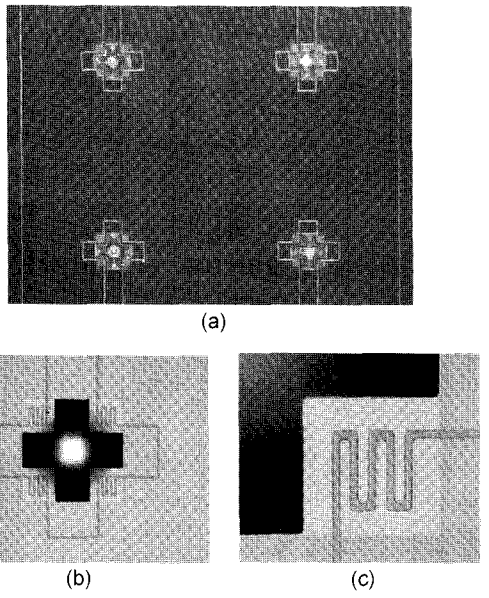
teristics for structural components in the sensor arrays as well as to be a hard mask for wet anisotropic etching of silicon. The LSN layer deposited by LPCVD is able to form a free standing structure alone. This LPCVD process has proven to produce a high integrity, repeatable, controllable film ideal for many microfabrication applications. A stack of the LSN films with embedded Ta (Tantalum) metal line has been fabricated to make use of a confining layer to keep the individually addressable microspheres and localized heaters in a chip-based sensor array.

2. Experiment

A DSP (double-side polished) 4-inch P-type (100) single crystal silicon wafer was used as a substrate material. After clean procedure, a LSN film was deposited by LPCVD with dichlorosilane (SiH_2Cl_2, DCS) as a source of silicon and ammonia (NH_3) as a source of nitrogen with flow rates of 60 and 15 sccm respectively at a pressure of 230 mTorr and a temperature of 840 °C while a stoichiometric silicon nitride film has been deposited with gas flow ratio (DCS/NH_4) of 2/7. The thickness of the film was 2000 Å. It was determined from step height measurements by α-step stylus profilometer. Deposition of Ta film was followed by reactive magnetron sputtering of the Ta target with purity of 99.95 %. Argon (Ar) was used as sputtering gas with fixed flow rate of 20 sccm. The base pressure of the chamber was 5×10^{-7} Torr. The deposition pressure and the sputtering power were maintained at 10 mTorr and 1.1 kW respectively. No intentional substrate heating was performed. The thickness of Ta was about 5000 Å. A serpentine metal line with width of 10 μm was patterned for future heater lines. After Ta patterning, the LSN layer was deposited again with same operational parameters with the thickness of 5000 Å. The cross opening with 200 μm width was patterned on the stack of films as shown in Fig. 2. After removal of the cross patterned films the silicon substrate was micromachined

Table 1. Current taste chip analyte summary

Analyte	Class	Sample mixture	Assay type	Status	Ref.
H(+)	pH	aqueous	pH indicator	optimized, fully tested, compared with standards, ANN studies	6, 7
glucose	sugar	aqueous	enzyme assay	optimized, fully tested	10
ATP, GTP, AMP	biological cofactor	aqueous	dye displacement assay	optimized, fully tested, PC studies	11
CRP	protein, cardiac risk factor	human serum, saliva	immunology	optimized, fully tested, compared with standards	12
DNA oligos	generic tests	aqueous	hybridization	optimized, fully tested	13



(a) (b) (c)

Fig. 2. (a) A 2 × 2 sensor array with heaters in the free standing layers on the micromachined cavities where the microspheres were localized, (b) A microphotography of one cell of the 2 × 2 sensor array, and (c) One quaternary free standing layer with embedded heaters.

by KOH etching with undercutting to form the pyramid shape micro cavity as shown in Fig. 2(b).

3. Results and Discussion

The stress remains in thin films after deposition on substrates. It may influence on the properties of the film, which may affect performance and integrity of microdevices. One source of the stress is caused by the mismatch in thermal expansion coefficient between the film and the substrate, introduced on cooling from processing temperature. The second source is the intrinsic stress[4]. Compressive stress can cause buckling of the film whereas high tensile stress may produce cracking/fracturing of the film[4,14]. To obtain a relatively large self-supporting area with sufficient mechanical stability on a silicon substrate Han and Vlklein utilized two silicon nitride layers cladding a silicon dioxide layer to form the membranes since these sandwich structures compensate the compressive and tensile stresses of the films[2,15].

One of the experimental techniques for measuring stress in a thin film on the substrates is curvature measurement of the substrate before and after deposition of a thin film. To convert the curvature to stress, the most frequently used relationship is the Stoney equation, given as:

$$\sigma = \frac{1}{6E(1-\nu)} \frac{t_s}{t_f} \left(\frac{1}{R} - \frac{1}{R_0} \right) \quad (1)$$

where $E/(1-\nu)$ is the biaxial elastic modulus of the substrate, t_s is the thickness of the substrate, t_f is the thickness of the film, R_0, R are the reference radius of curvature and the final radius of curvature (in this case after film deposition), respectively[14]. The residual stress of a stoichiometric silicon nitride film deposited by LPCVD is reported to be 1,200 MPa (tensile stress)[5]. The LSN film was deposited by the same method, LPCVD process, on a silicon substrate with an NH_3/DCS ratio of 15/60 at the temperature of 840 °C and the pressure of 230 mTorr. The residual stress was measured with the laser curvature method. The average stress of the LSN was 207.7 MPa (tensile stress). It is about 6 times smaller than that of the stoichiometric silicon nitride. Therefore, the LSN film is relatively stable. The free standing structure of the LSN film is shown in Fig. 2.

Typical materials for the microspheres are polystyrene-polyethylene glycol (small molecule, anions, cations) and agarose (enzymes, proteins, antibodies). For both types of the microspheres, they swell in size upon exposure to the fluids. For the polystyrene-polyethylene glycol microsphere, a typical size of about 150 μm in diameter in a dry state changes to about 230 μm in diameter in a wet state. The micromachined cavities allow for the expansion of the microspheres and avoid problems incurred by attaching the polymer to a platform. However, the microspheres are easy to escape from their proper location because of their swelling and floating properties of the microspheres . Hence, a confining structure (cover glass, Teflon fluid package) has been used[7,8]. Fig. 3 shows swelling of the microspheres.

Fig. 2(a) shows a top view of a 2 × 2 sensor array having the LSN layers with embedded Ta lines for heating source above the micromachined cavities where the microspheres are located. Fig. 2(b) shows a cell of the array with four free standing LSN layers on a single micromachined cavity. One free standing layer of the cell which shows no notable deflection through the microscope in Fig. 2(c). Hence these free standing lay-

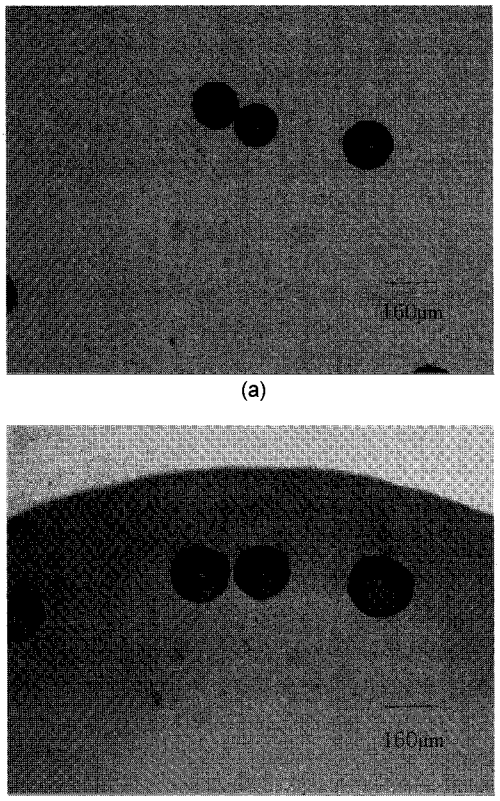


Fig. 3. Swelling of the microspheres; (a) before exposure to fluid and (b) after exposure to the fluid.

ers including the LSN films can play roles as confining structure for the microspheres and localized heating sources. The thermal generator can be used in PCR (Polymerase Chain Reaction) to make a huge number of copies of genes and protein incubation in the electronic tongue system.

4. Conclusion

In summary, the free standing low stress silicon nitride layer has been fabricated by LPCVD process by changing ratio of source gases. This LSN film has residual stress 6 times lower than that of the stoichiometric silicon nitride film. The films were shown to have desirable characteristics for the free standing structure that would be utilized to confine the microshperes in the proper locations. Also, The LSN layers embedded Ta line may be used as localized heat source for DNA amplification and protein incubation.

References

[1] H. C. Lim, B. Schulkin, M. J. Pulickal, S. Liu, R. Petrova, G. Thomas, S. Wagner, K. Sidhu, and J.F. Federici, "Flexible membrane pressure sensor", *Sens. Actuators A*, vol. 119, pp. 332-335, 2005.

[2] J. Han, "Fabry-perot cavity chemical sensors by silicon micromachining techniques", *Appl. Phys. Lett.*, vol. 74, pp. 445-447, 1999.

[3] M. A. Gritz, M. Metzler, J. Moser, D. Spencer, and G. D. Boreman, "Fabrication of air bridges using electron beam lithography", *J. Vac. Sci. Technol. B*, vol. 21, pp. 332-334, 2003.

[4] P. J. French, P. M. Sarro, R. Malle, E. J. M. Fakkeldij, and R.F. Wolffenbuttel, "Optimization of a low-stress silicon nitride process for surface-micromachining applications", *Sens. Actuators A*, vol. 58, pp. 149-157, 1997.

[5] B. C. S. Chou, J.-S. Shie, and C.-N. Chen, "Fabrication of low-stress dielectric thin-film for microsensor applications", *IEEE Electron Device Letters*, vol. 18, pp. 599-601, 1997.

[6] J. J. Lavigne, S. Savoy, M. B. Clevenger, J. E. Ritchie, B. McDoniel, S.-J. Yoo, E. V. Anslyn, J. T. McDevitt, J. B. Shear, and D. P. Neikirk, "Solution-based analysis of multiple analytes by a sensor array: Toward the development of an 'electronic tongue'", *J. Am. Chem. Soc.*, vol. 120, pp. 6429-6430, 1998.

[7] A. Goodey, J. Lavigne, S. Savoy, M. Rodriguez, C. Theodore, A. Tsao, G. Simmons, J. Wright, S.-J. Yoo, Y. Sohn, E. Anslyn, J. Shear, D. Neikirk, and J. McDevitt, "Development of multianalyte sensor arrayscomposed of chemical derivatized polymeric microspheres localized in micromachined cavities", *J. Am. Chem. Soc.*, vol. 123, pp. 2559-2570, 2001.

[8] Y.-S. Sohn, E. V. Anslyn, J. T. McDevitt, J. B. Shear, and D. P. Neikirk, "Multianalyte sensor array using capillary-based sample introduction fluidic structure: Toward the development of an 'electronic tongue'", *J. Kor. Sens. Soc.*, vol. 13, pp. 378-382, 2004.

[9] B. H. Park, Y. S. Park, Y.-S. Sohn, and D. P. Neikirk, "Fabrication of bead size sorting chip for chemical array sensor", *Proceedings of SPIE-Smart Sensors, Actuators, and MEMS*, Maspalomas, Gran Canaria, pp. 303-313, Spain, 2003.

[10] T. E. Curey, A. Goodey, A. Tsao, J. Lavigne, Y. Sohn, J. T. McDevitt, E. V. Anslyn, D. Neikirk, and J. B. Shear, "Characterization of multicomponent monosaccharide solutions using an enzyme-based

sensor array", *Analytical Biochemistry*, vol. 293, pp. 178-184, 2001.

[11] S. C. McCleskey, M. J. Griffin, S. E. Schneider, J. T. McDevitt, and E.V. Anslyn, "Differential receptors create patterns diagnostic for ATP and GTP", *J. Am. Chem. Soc.*, vol. 125, pp. 1114-1115, 2003.

[12] N. Christodoulides, M. Tran, P. N. Floriano, M. Rodriguez, A. Goodey, M. Ali, D. Neikirk, and J. T. McDevitt, "A microchip-based multianalyte assay system for the assessment of cardiac risk", *Analytical Chemistry*, vol. 74, pp. 3030-3036, 2002.

[13] M. Ali, R. Kirby, A. Goodey, A. Ellington, D. P. Neikirk, and John T. McDevitt, "DNA hybridization and discrimination of single-nucleotide mismatches using microbead arrays", *Analytical Chemistry*, vol. 75, pp. 4732-4739, 2003.

[14] Z. B. Zhao, J. Hershberger, S. M. Yalisove, and J. C. Bilello, "Determination of residual stress in thin films: a comparative study of X-ray topography versus laser curvature method", *Thin Solid Film*, vol. 415, pp. 21-31, 2002.

[15] F. Vlklein, "Thermal conductivity and diffusivity of a thin film SiO_2-Si_3N_4 sandwich system", *Thin Solid Films*, vol. 188, pp. 27-33, 1990.

손 영 수 (Young-Soo Sohn)

- 1994년, 경북대학교 물리학과 졸업(이학사)
- 1997년, 경북대학교 대학원 물리학과 졸업 (이학석사)
- 2001년, The University of Texas at Austin, Dept. of Electrical & Computer Engineering(공학박사)
- 2001년 ~ 2002년, University of Cincinnati (선임연구원)
- 2003년 ~ 2005년, The Univ. of Texas at Austin(선임연구원)
- 2005년 ~ 현재, 대구경북과학기술연구원 (선임연구원)
- 주관심분야 : 마이크로 센서, 반도체 소자, 나노 공정