LOW-TEMPERATURE CHEMICAL-VAPOR-DEPOSITION OF SILICON NITRIDE

H. Kanoh, O. Sugiura, S. Fujioka, Y. Aramaki, T. Hattori, M. Matsumura

► To cite this version:

H. Kanoh, O. Sugiura, S. Fujioka, Y. Aramaki, T. Hattori, et al.. LOW-TEMPERATURE CHEMICAL-VAPOR-DEPOSITION OF SILICON NITRIDE. Journal de Physique IV Proceedings, 1991, 02 (C2), pp.C2-831-C2-837. 10.1051/jp4:1991298 . jpa-00249890

HAL Id: jpa-00249890

<https://hal.science/jpa-00249890>

Submitted on 1 Jan 1991

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

LOW-TEMPERATURE CHEMICAL-VAPOR-DEPOSITION OF SILICON NITRIDE

H. KANO, O. SUGIURA, S. FUJIOKA*, Y. ARAMAKI*,
T. HATTORI* and M. MATSUMURA

*Department of Physical Electronics, Tokyo Institute of
Technology, Oh-okayama, Meguro-ku, Tokyo 152, Japan*

**Department of Electrical and Electronic Engineering,
Musashi Institute of Technology, Tamazutsumi, Setagaya-ku, Tokyo
158, Japan*

Abstract: Low-temperature CVD method has been investigated for silicon-nitride films by using higher silanes and hydrazine aiming at thin-film transistor application. The deposition temperature has been reduced to as low as 350°C, i.e., by about 400°C lower than the typical temperature. Atomic N/Si ratio was more than 4/3, i.e., the film was stoichiometric SiN, and hydrogen content was as high as 20 atomic%. Breakdown field strength, specific resistivity and MIS interface state density were about 6MV/cm, $6 \times 10^{13} \Omega \text{cm}$ and $1 \times 10^{11} \text{cm}^{-2} \text{eV}^{-1}$, respectively.

1. Introduction

Much attention has been paid recently to low-temperature (less than 400°C) deposition method of silicon-nitride (SiN), since the SiN film deposited at low-temperatures is useful as a passivation layer for VLSI chips and a gate insulator for amorphous-silicon thin-film transistors (a-Si TFTs) in flat-panel displays./1/ Plasma-enhanced CVD (PCVD)/2/ is the most representative method for low-temperature deposition of SiN, where silane (SiH_4) and ammonia (NH_3) are the commonly used source gases. This is because plasma can crack the thermally stable source molecules to reduce drastically the deposition temperature from as high as 800°C to less than 250°C. The PCVD method, however, has serious shortcomings; (1) high energy electrons and ions generated in plasma introduce damages in the deposited SiN film, (2) plasma-polymerization generates many flakes in the PCVD chamber, resulting in dense pin-holes in the film, and (3) through-put is low since a number of substrates can not be loaded in a stack-like manner into the PCVD chamber. Though these shortcomings are minor in a solar cell application, they cause serious problems in the TFT application. This is because the device impedance is as high as $10^{11} \Omega \text{cm}^2$ for TFTs while it is as low as $100 \Omega \text{cm}^2$ for solar cells.

Since these shortcomings are caused by plasma, plasma-free deposition, i.e., thermal-CVD/3/ will solve all problems mentioned above. This method, however, has been considered for a long time difficult to be applied into the a-Si TFT process since high temperature is needed to decompose SiH_4 and NH_3 .

Yoshioka and Takayanagi reported/4/ that by using hydrazine (N_2H_4) instead of NH_3 the SiN CVD temperature can be reduced to 600°C, i.e., by about 200°C lower than the typical temperature. This temperature, however, is still too high to form the VLSI passivation layer or the a-Si TFT gate insulator. Since deposition kinetics are governed by decomposition mechanism of SiH_4 but not by that of N_2H_4 , the temperature will be reduced further by replacing SiH_4 to higher-silanes such as disilane (Si_2H_6) or trisilane (Si_3H_8)/5,6,7,8/, which are commercially available now-a-day.

We have thus investigated the low-temperature CVD of SiN and a-Si films using higher-silanes and hydrazine. High performance CVD a-Si/SiN TFT has been demonstrated recently/9/, and the optimum CVD conditions for the a-Si film have

been reported elsewhere./10,11/ In this paper, we present for the first time the low-temperature SiN CVD characteristics and its film properties.

2. Deposition System

Deposition system used in this work is shown schematically in Fig. 1. The reaction chamber was of a pyrex tube with a diameter of 10cm and a length of 50cm. It was evacuated by a rotary pump. Samples were heated by a ceramic heater placed at the center of the chamber and the substrate temperature was monitored by a thermocouple.

Source gases are Si_2H_6 or Si_3H_8 and N_2H_4 , whose decomposition temperatures are considerably lower than those of SiH_4 and NH_3 , respectively. Since N_2H_4 is liquid at room temperature, it was introduced into the chamber by using N_2 as carrier gas. Flow rate of N_2 carrier gas was fixed at 40sccm, and the N_2H_4 flow rate was changed by adjusting the bubbler temperature between 25°C and 60°C . The carrier gas was introduced from the top of the chamber to establish a laminar flow condition. The gas was pre-heated to 575°C just at the inlet in order to suppress cooling of the substrate surface. The flow rate of Si_2H_6 (or Si_3H_8) gas was fixed at 0.6sccm (or 0.3sccm). The gas was blown over the substrate surface directly. The chamber was pumped to less than 5mTorr before the deposition, and the pressure in the chamber during the deposition was kept constant by adjusting an exhaust valve.

Fig. 1. Schematic diagram of the CVD system.

3. Deposition Characteristics

Deposition rate is shown by open circles in Fig. 2 as a function of reciprocal substrate temperature T_{sub} . The N_2H_4 flow rate and the total pressure were kept at 4.85sccm and 100Torr, respectively. A Si_2H_6 - N_2H_4 gas mixture can deposit the SiN film at substrate temperatures of as low as 400°C . The temperature reduction was more than 200°C . The logarithmic deposition rate was proportional to the reciprocal temperature for temperatures of less than 450°C , and its activation energy was 32kcal/mol which is approximately equal to energy of N-N bond breaking/12/. Above 450°C , deposition rate had a tendency of saturation.

We have attempted to deposit SiN films at lower temperatures by using Si_3H_8 instead of Si_2H_6 . Results are also shown as closed circles in Fig. 2 where the N_2H_4 flow rate was 4.85sccm. The deposition temperature was reduced further. But the activation energy was also 32kcal/mol, the refractive index was more than 2.1, and the film resistivity was low. Thus we have concluded that the deposition kinetics were predominantly controlled by decomposition mechanism of hydrazine, and that the film is silicon-rich. For forming the good insulating SiN film at lower temperatures using trisilane, the new nitrogen source gas should be developed.

Fig. 2. Deposition rate as a function of reciprocal substrate temperature for $\text{N}_2\text{H}_4\text{-Si}_2\text{H}_6$ and $\text{N}_2\text{H}_4\text{-Si}_3\text{H}_8$.

4. Film Properties

Compositional properties of the SiN films formed from a $\text{Si}_2\text{H}_6\text{-N}_2\text{H}_4$ gas mixture have been evaluated by infrared absorption spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS). Electrical properties of the film have been also evaluated from view points of breakdown field strength, resistivity, dielectric constant and MIS interface state density.

4-1. Effects of $\text{N}_2\text{H}_4/\text{Si}_2\text{H}_6$ Flow Rate Ratio

The Si_2H_6 flow rate was kept constant at 0.6sccm and the N_2H_4 flow rate was varied from 0.75sccm to 4.85sccm by changing the bubbler temperature. The deposition temperature was fixed at 485°C . Since the total flow rate is changed with the N_2H_4 flow rate and a gas volume is increased to 3 times by decomposing N_2H_4 to N_2 and H_2 , we have changed the total pressure to keep a residence time constant. The chamber pressure was thus between 76Torr and 100Torr. Detailed deposition conditions are shown in Table I.

Table I

T_{sub}	: 485°C
Si_2H_6	: 0.6sccm
N_2H_4	: 0.75~4.85sccm
P	: 76~100Torr

4-1-1. Chemical Properties

The deposition rate and the refractive index are shown in Fig. 3 as a function of the $\text{N}_2\text{H}_4/\text{Si}_2\text{H}_6$ flow rate ratio R. The etching rate by buffered HF solution ($\text{NH}_4\text{F}:\text{HF}=6:1$) at 20°C is also plotted in the figure.

The deposition rate decreased steadily with increasing R. This may be caused by reduced number of deposition sites at the SiN surface during the deposition, since H atoms left from N_2H_4 molecules will effectively terminate the Si and N dangling bonds at the surface. The refractive index was 2.15 and the etching rate was 0.1nm/sec at low R of 1.25. With increasing R, the refractive index decreased rapidly, and was saturated at 1.83 at $R=3$. With increasing R, the etching rate increased, it took a peak value at $R=3$, then changed to decrease and was saturated at 2.4nm/min for R larger than 5. The etching rate is large and the refractive index is small compared with typical values of the CVD SiN film./13/ But these values are approximately the same to those of the good PCVD SiN film./14/

The atomic component of SiN films evaluated by the photoelectron spectrum intensity ratio N_{1s}/Si_{2p} and O_{1s}/Si_{2p} of XPS (S.S.I.:SSX-100) were shown in Fig. 4. The atomic ratio N/Si increased rapidly from 0.74 with increasing R, reached the stoichiometric value of 1.33 at R=5 and then saturated. The O/Si ratio decreased rapidly with increasing R for small R and was saturated at 0.05 for R larger than 3. This does not mean that there was dense oxygen in the deposited film since we must take into account native oxide formed at the surface during storage of the sample. It should be noted that RBS measurement showed no clear peak of oxygen for the films deposited under R>3 conditions.

Fig. 3. Deposition rate, refractive index and etching rate by buffered HF solution as a function of N_2H_4/Si_2H_6 flow rate ratio R.

Fig. 4. Atomic ratio of N/Si and O/Si as a function of N_2H_4/Si_2H_6 flow rate ratio R. The atomic ratio were evaluated by XPS.

4-1-2. Electrical Properties

MIS structure was formed on n-type crystal-silicon wafers having a resistivity of $3\sim 6\Omega\text{cm}$. SiN thickness was about 100nm. Aluminum electrode area was $4.3\times 10^{-4}\text{cm}^2$. The measured $I-E^{1/2}$ characteristics are shown in Fig.5 for several R values, where I is the current density crossing the SiN film and E the electric field strength across the film. At R=1.25, the film did not show good blocking characteristics and the resistivity was as low as $6\times 10^{13}\Omega\text{cm}$. With increasing R value the characteristics became similar to the conventional form reported by many workers, i.e., the current took a very low value for low E and increased exponentially with E for high E./15/

The resistivity and the breakdown field strength are shown in Fig. 6 as the function of R. Resistivity defined by the leakage current density at $E=1\text{MV/cm}$, was $6.0\times 10^{13}\Omega\text{cm}$ for R=1.25. It increased rapidly with R and was saturated at $6.4\times 10^{15}\Omega\text{cm}$ for R>3. The breakdown field strength, defined by the field strength at $1\mu\text{A/cm}^2$ leakage current, was 1.8MV/cm at R=1.25, increased rapidly with R and took more than 6.0MV/cm at R=8.1.

MIS characteristics have been measured at a frequency of 100kHz. It showed a typical high-frequency curve. Dielectric constant estimated from accumulation conditions of the MIS capacitor are shown also in Fig. 6. It was 8.5 at $R=1.25$, decreased with increasing R , and saturated at 6.5 for high R . The hysteresis voltage width of the C-V curve was 2.4V at $R=1.25$ and decreased with increasing R . There was no apparent hysteresis for the film deposited at $R=8.1$. The interface state density distribution was of a V-shaped form and the minimum value was $1.0 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ at $R=1.25$, decreased with increasing R , and was $1.0 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ at $R=8.1$. These results mean that electrical properties of the SiN film are improved by increasing R . Dominant origin of this improvement is that the film becomes stoichiometric, resulting in the reduction of deep trap density.

It was concluded that the CVD SiN film deposited at $R=8.1$ and 485°C have electric properties better than the PCVD SiN film. The high performance a-SiTFTs have been demonstrated using the CVD SiN gate formed under these conditions.^{9,10/}

Fig. 5. $I-E^{1/2}$ characteristics estimated by MIS capacitor for the $\text{N}_2\text{H}_4/\text{Si}_2\text{H}_6$ flow rate $R=1.25$, 3 and 8.1.

Fig. 6. Breakdown field strength, resistivity and dielectric constant as a function of $\text{N}_2\text{H}_4/\text{Si}_2\text{H}_6$ flow rate ratio R .

4-2. Effects of Deposition Temperature

The lower deposition temperature is still preferable for applying the CVD method into a-SiTFT arrays on large glass substrate such as 10-inches in diagonal size since thermal distortion becomes serious in the large substrate. Thus we have investigated effects of deposition temperature on the film properties. The deposition conditions are tabulated in Table II. The Si_2H_6 and N_2H_4 flow rates were kept constant at 0.6sccm and 4.85sccm, respectively. The pressure was 100 Torr.

Table II

T_{sub}	: $400 \sim 525^\circ\text{C}$
Si_2H_6	: 0.6sccm
N_2H_4	: 4.85sccm
P	: 100Torr

Fig. 7. Atomic ratio of N/Si and O/Si, and hydrogen content as a function of deposition temperature. The atomic ratio and the hydrogen content were evaluated by XPS and FTIR, respectively.

Fig. 8. Breakdown field strength, resistivity and dielectric constant as a function of deposition temperature.

4-2-1. Chemical Properties

The deposition rate was already shown in Fig. 2 as a function of deposition temperature. The O/Si and N/Si atomic ratios estimated from XPS are shown in Fig. 7. The N/Si ratio first increased from 1.27 with increasing the temperature and then started to decrease for high temperature more than 475°C. The maximum ratio was 1.33, i.e., the film is of stoichiometric (Si_3N_4). The O/Si ratio was as high as 0.15 for the film deposited at 400°C and decreased steadily with the temperature.

Hydrogen content has been evaluated from FTIR spectrum. There were large peaks at 2160cm^{-1} and 3350cm^{-1} , which can be attributed to Si-H and N-H bondings, respectively. Hydrogen content was calculated by using a formula proposed by W.A.Lanford./16/ The results were also shown in Fig. 7. At the deposition temperature of 400°C, total hydrogen content was 15atomic% and number of Si-H bonds was approximately the same with that of N-H bonds. With increasing the temperature, the number of Si-H bonds decreased gradually due to thermal breaking of Si-H bond, but the number of N-H bonds increased rapidly due to the increased N content. Thus total hydrogen content was increased with temperature. The N-H bondings, however, begin to break at about 475°C since N-H bonding energy of 85kcal/mol is only a little larger than Si-H bonding energy of 70.4kcal/mol./17,18/ Thus the hydrogen content took the highest value of about 21atomic% at the temperature of 475°C and it decreased rapidly with temperature.

4-2-2. Electrical Properties

The resistivity, the breakdown field strength and dielectric constant are shown in Fig. 8 as the function of the deposition temperature. The resistivity was

$1.2 \times 10^{15} \Omega \text{cm}$ at 400°C . And it increased with increasing the temperature and took $3.4 \times 10^{15} \Omega \text{cm}$ at 525°C . The breakdown field strength was 6.5MV/cm at 400°C , decreased with increasing the temperature and took 6MV/cm at 525°C . The dielectric constant increased from 5.7 to 6.6 with increasing the temperature from 400°C to 525°C , respectively. The fact that the breakdown field strength was reduced with increasing the temperature does not mean that the high temperature results in inferior SiN film properties. High breakdown field strength at low temperature is caused by dense oxygen in the film, i.e., the film was SiON. It should be concluded that the film deposited at 400°C has still the similar properties with the PCVD SiN film, and that it is also acceptable for the TFT gate insulator./9/

5. Conclusion

Higher silanes and hydrazine gas mixture reduces the SiN CVD temperature to less than 350°C . The film contains hydrogen of more than 15 atomic% and becomes stoichiometric by increasing either the deposition temperature or the $\text{N}_2\text{H}_4/\text{Si}_2\text{H}_4$ gas flow rate ratio.

Since the CVD SiN film has good electric properties as the PCVD film, the low temperature CVD method is very attractive due to following reasons. Firstly, there is only a few particles in the chamber, which cause the most serious problem in the present a-Si TFT process. Secondly, SiN can be deposited simultaneously on many substrates in the chamber./19/ These advantages of CVD method, i.e., high yield and high throughput make the method very attractive for the a-Si TFTs process.

Acknowledgments

The authors would like to express their thanks to Showa-Denko for preparing trisilane.

References

- /1/ Tannas E.L., IEEE Spectrum, 26 (1989) 34.
- /2/ LeComber G.P., W.E.Spear and A.Ghaith, Electron. Lett., 15 (1979) 179.
- /3/ Sze M.S., "VLSI Technology", McGraw-Hill Book Company, (1983) 119.
- /4/ Yoshioka S. and Takayanagi S., J. Electrochem. Soc., 114 (1967) 962.
- /5/ Gau C.S., Weinberger R.B. and A.G.MacDiarmid, Appl. Phys. Lett., 39 (1981) 436.
- /6/ Ellis B.F. and Gordon G.R., J. Appl. Phys., 54 (1983) 5381.
- /7/ Chu L.T., Chu S.S. and Ang T.S., J. Appl. Phys., 59 (1986) 1319.
- /8/ Breddels A.P., Kanoh H., Sugiura O. and Matsumura M., Electron. Lett., 24 (1989) 1637.
- /9/ Kanoh H., Breddels A.P., Sugiura O. and Matsumura M., IEEE Electron. Device Lett., 11 (1990) 258.
- /10/ Kanoh H., Breddels A.P., Sugiura O. and Matsumura M., Jpn. J. Apply. Phys., 29 (1990) 2358.
- /11/ Breddels A.P., Kanoh H., Sugiura O. and Matsumura M., Jpn. J. Apply. Phys., 30 (1991) 233.
- /12/ Jones K., "The Chemistry of Nitrogen", Pergamon Press, (1973) 164.
- /13/ Kern W. and Rosler S.R., J. Vac. Sci. & Technol., 14 (1977) 1082.
- /14/ van den Ven T.G.P.E., Solid state Technol., 24 (1981) 167 (4).
- /15/ Sze M.S., "Physics of Semiconductor Devices", Wiley, (1981) 402.
- /16/ Lanford A.W., J.Appl.Phys. 49(1987)2473.
- /17/ Jones K., "The Chemistry of Nitrogen", Pergamon Press, (1973) 164.
- /18/ Rochow G.E., "The Chemistry of Silicon", Pergamon Press, (1973) 121.
- /19/ Meakin D., Ferry A., Palmer D. and Saunders M., Digest of Technical Papers of 1989 Int'l. Symp. of Soc. Inform. Display, Baltimore, (1989) 159.