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Plasma-Enhanced Chemical Vapor Deposition of Silicon Nitride

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The optimum condition of plasma-enhanced chemical vapor deposition to deposite silicon nitride (SiN_x) film and its application as a gate insulator of a-Si thin-film transistor (TFT) have been investigated. The internal stress of SiN_x in the range of 4.3×10^9 dyn/cm^2 tensile to 8.0×10^9 dyn/cm^2 compressive is found to be controllable by changing the ratio of H_2 and N_2 in the source gases without affecting the optical band gap. Satisfactory TFT characteristics and high reliability are realized by using a gate insulator of SiN_x having either stoichiometric or N-rich composition which shows the large optical band gap.

KEYWORDS: plasma-enhanced CVD, silicon nitride, internal stress, composition, TFT, reliability

§1. Introduction

Silicon nitride (SiN_x) thin-films deposited by plasma enhanced chemical vapor deposition (PECVD) are widely applicable as protection films of semiconductor devices and gate insulator films of thin-film transistors (TFTs) to drive liquid crystal panels, and so on. The characteristics of such SiN_x films are governed more strongly by the deposition apparatus and conditions than are those deposited by thermal CVD methods, and therefore, have many unknown factors.

There have been several papers[1-4] reporting on the chemical compositions and physical properties of SiN_x films deposited by PECVD methods using SiH_4 and NH_3 as source gases.

These papers reported that the silicon nitride films prepared by conventional PECVD methods employing a high-frequency RF power source of more than several MHz showed tensile stresses while those prepared using a low-frequency RF power source such as 50 kHz showed compressive stresses.

In thin-film device manufacturing, the internal stress of the thin film is a highly important factor because an excessive tensile stress may cause cracking in the device while an excessive compressive stress may invite peeling of the deposited thin film. Moreover, the performance and reliability of TFT using SiN_x gate insulator film are governed largely by its chemical composition.

This paper reports on the experimentally determined relationships between SiN_x deposition conditions and internal stresses, in addition to the relationship between chemical compositions and performance of a-Si TFT of which the gate insulator film is made of SiN_x when it is used as a switching element of a liquid crystal display panel.

§2. Experiments

The SiN_x films were deposited on either high-resistivity silicon or quartz substrates by using a capacity-coupled plasma CVD apparatus employing a 13.56 MHz RF power source under various conditions of gas-flow rate, pressure, substrate temperature, and discharge RF power, which are shown in Table I.

The refractive index and the optical band gap (E_{gopt}) were measured for the evaluation of SiN_x characterization. The optical band gap is defined as photon energy where the absorption coefficient is 5×10^4 cm^{-1}. The chemical composition of film was determined by Rutherford backscattering analysis (RBS), proton recoil detection (PRD) and electron spectroscopy for chemical

Table I. Deposition conditions.

Apparatus frequency cathode area	 13.56 MHz 900 cm^2
Source gases SiH_4 NH_3 N_2 H_2	 15 ~ 18 sccm 72 ~ 90 sccm ~ 300 sccm ~ 300 sccm
Pressure	0.9 ~ 1.2 Torr
Substrate Temp.	290 ~ 320°C
RF power	100 ~ 400 W

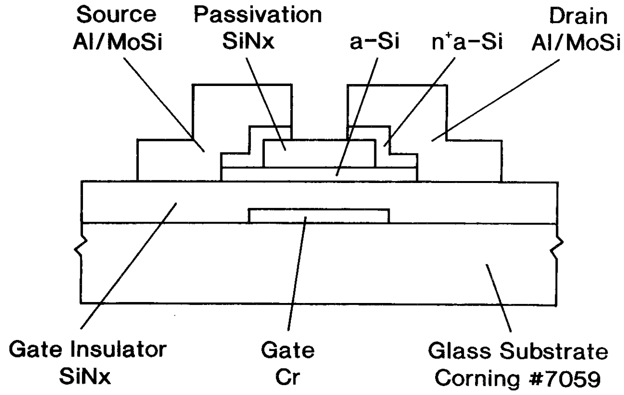


Fig. 1. Schematic configuration of a-Si TFT.

analysis (ESCA). The hydrogen bond and spin density were evaluated by an IR method and by ESR, respectively.

The internal stress was calculated from the change in the curvature of the substrate on which SiN_x film was deposited, and its etching rate was determined using a buffered HF solution (BHF(1:6)). The characteristics of TFT were evaluated by fabricating inverse-staggered TFTs of which the channel was passivated by the SiN_x film, as shown in Fig. 1.

§3. Experimental Results

3.1 *Effects of deposition condition on SiN_x film property*

3.1.1 *Dependency on RF power*

Figure 2 shows a plot of internal stresses of prepared SiN_x films when the RF power is varied in the range 100–400 W while keeping the gas-flow rate, pressure, and the substrate temperature constant. The gases used are either of a SiH_4, NH_3 and H_2 system gas or a SiH_4, NH_3 and N_2 system gas. As shown in Fig. 2, the internal stresses of SiN_x film which is tensile at low RF power (~250 W) changes toward compressive with increasing RF power when the SiH_4, NH_3 and H_2 system gas is used. At RF power of 400 W, the stress is a compressive one of 2.8–3.8 × 10^9 dyn/cm^2. However, when the SiH_4, NH_3 and N_2 system gas is used, the internal stress is consistently tensile (3.1–4.5 × 10^9 dyn/cm^2). This is true even with a higher RF power, thus indicating very little dependency on the RF power.

Figure 3 shows the dependence of other characteristics of SiN_x film on the RF power. It shows decreases of both the refractive index and the optical band gap with increase in RF power. This can be interpreted as a decrease of the silicon to nitrogen (Si/N) ratio in the SiN_x film for a higher RF power, and this means that the SiN_x film has turned into a nitrogen-rich film. Moreover, the fact of lower etching rate of such a film in BHF implies that the film density increases with a higher RF power.

3.1.2 *Effects of mixture ratio of H_2 and N_2*

The stress of SiN_x films is compressive when deposited in the SiH_4, NH_3 and H_2 system gas with a higher RF power (300 W ~) while it is tensile when deposited in the SiH_4, NH_3 and N_2 system gas with a higher RF power. The ratio of $H_2/(H_2+N_2)$ is varied by holding the gas flow rates of SiH_4 and NH_3 at constant. Figures 4 and 5 show the results.

As shown in Fig. 4, the stress of the films changes in the range of 4.3×10^9 dyn/cm^2 tensile to 8.0×10^9 dyn/cm^2 compressive when the ratio of $H_2/(H_2+N_2)$ increases. Figure 5 shows that increasing the ratio of $H_2/(H_2+N_2)$ leads to an increase in the refractive index and a slight decrease of the optical band gap. The small change in optical bandgap implies that there is little change of the excessive Si in the film even if the stress in the film changes significantly.

3.2 *Composition of SiN_x film*

The content of hydrogen in the SiN_x film was determined by using PRD and IR methods, and the apportionment ratio between Si-H bonds and N-H bonds was calibrated from the IR absorption[4] of Si-H and N-H stretching frequencies at 2190 and 3350 cm^{-1}.

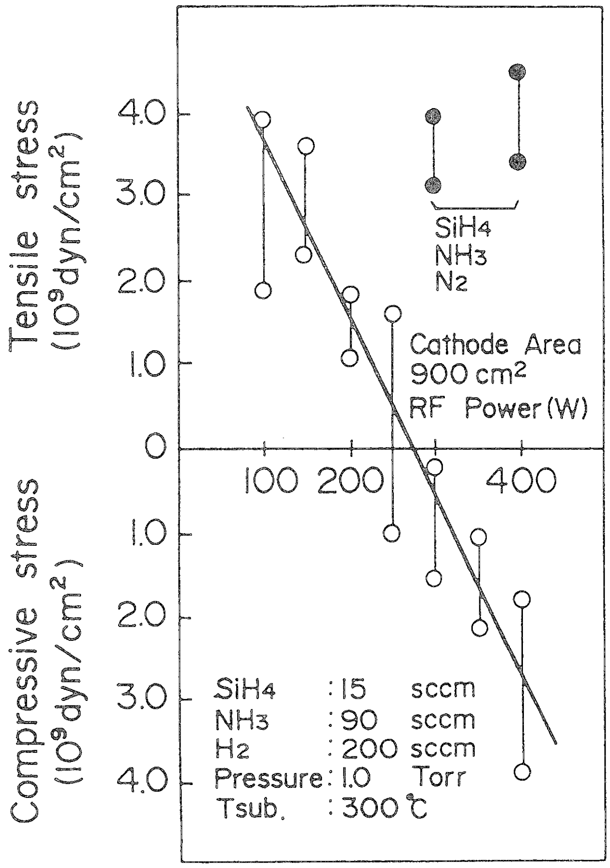


Fig. 2. Effect of RF power on the internal stress of SiN_x films.

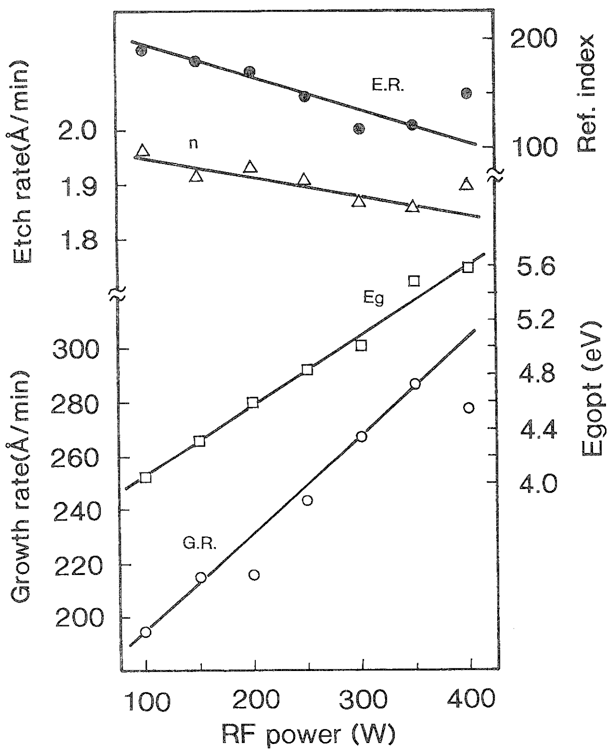


Fig. 3. Effect of RF power on the properties of SiN_x films.

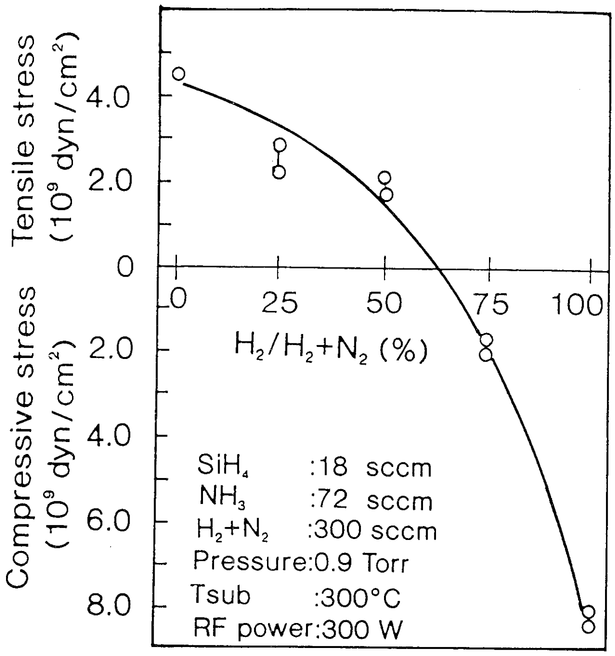


Fig. 4. Effect of the $H_2/(H_2+N_2)$ ratio on the internal stress of SiN_x films.

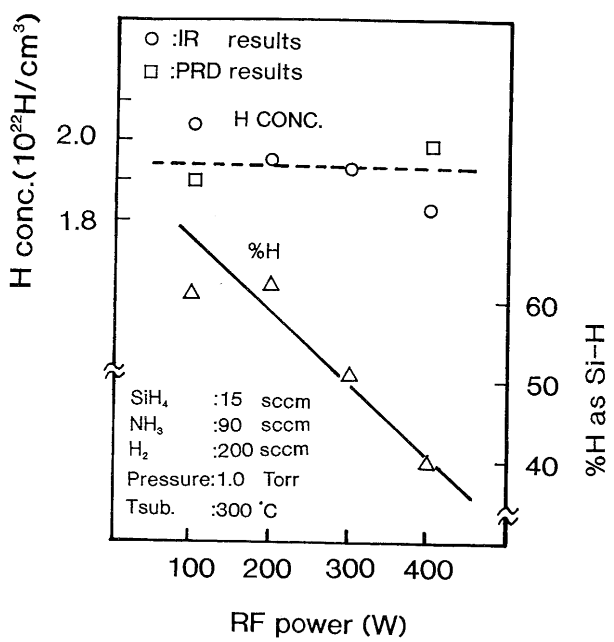


Fig. 6. Effect of RF power on the hydrogen content in SiN_x films and the ratio of hydrogen atoms bonded with silicon atoms.

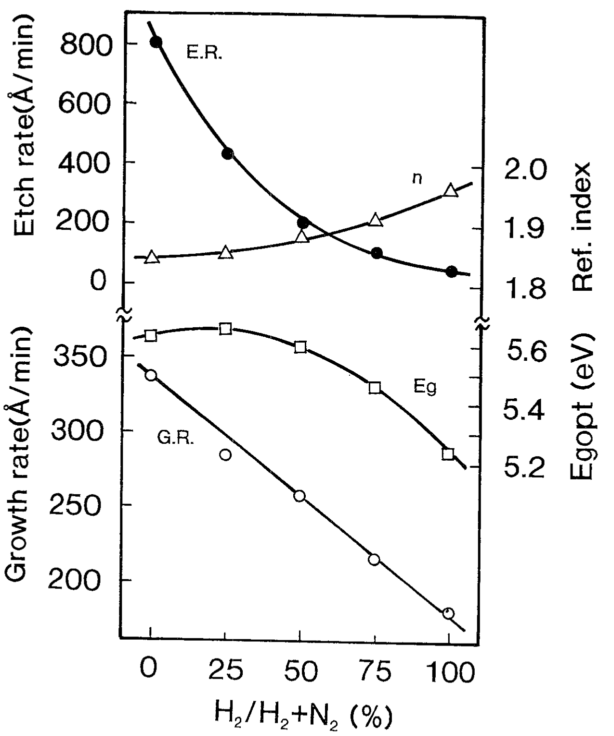


Fig. 5. Effect of the $H_2/(H_2+N_2)$ ratio on the properties of SiN_x films.

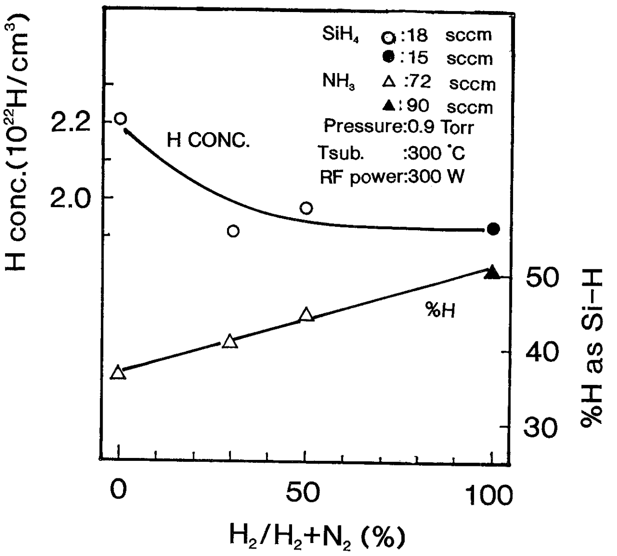


Fig. 7. Effect of the $H_2/(H_2+N_2)$ ratio on the hydrogen content in SiN_x films and the ratio of hydrogen atoms bonded with silicon atoms.

Figure 6 shows the effect of increasing RF power with the other conditions constant on the hydrogen content and the ratio of Si–H/N–H. The hydrogen content in the film is independent of RF power and the number of hydrogen atoms bonded with silicon atoms decreases at the higher RF power. This means that more dangling bonds in the film deposited by a lower RF power exist because of excessive silicon atoms in the film and inadequate hydrogen atoms with which to bond with, but the increased nitrogen atoms in the film deposited by a higher RF power bond with silicon atoms and the dangling bonds decrease substantially.

The ratio of $H_2/(H_2+N_2)$ is varied, keeping RF power constant (Fig. 7). Under these conditions, the content of hydrogen atoms in the film is nearly independent of the ratio of $H_2/(H_2+N_2)$, and the Si–H bonds increase slightly with increasing $H_2/(H_2+N_2)$ ratio. This correspoonds to the tendency of the slightly decreased optical band gap.

Table II shows the results of RBS and chemical compositions of the film determined by ESCA for the SiN_x films prepared under a typical deposition condition. The chemical composition is determined by curve-resolving the Si 2p peak into the respective peaks for the stoichiometric silicon nitride bond (Si_3N_4), the incompletely bonded chemical state of the silicon-nitrogen-hydrogen bond (SiNH), and the silicon-silicon bond (Si–Si) or silicon-hydrogen bond (Si–H) as shown in Fig. 8.

Table II also shows a significant dependence of the Si/N ratio in the deposited SiN_x on the RF power, depositing SiN_x films close to the stoichiometric ratio of 0.75 of Si_3N_4 or nitrogen-rich films with increasing RF power. However, the result of ESCA composition analysis shows that the composition ratio of stoichiometrically bonded Si_3N_4 is independent of the RF power, but shows an increase in incompletely bonded SiNH components and a decrease in Si–Si bonds at a higher RF deposition power, as shown in Fig. 8(a). Therefore, the optical band gap rises with increasing RF power.

Table II. Analytical results.

Conditions		E_{gopt} (eV)	RBS Si/N	ESCA (at.%)		
RF power	H_2/H_2+N_2			Si_3N_4	SiNH	Si–Si
100 W	100%	4.1	0.98	76	13	11
400 W	100%	5.6	0.78	76	15	9
300 W	50%	5.3	0.90	85	5	10
300 W	0%	5.5	0.75	90	0	10

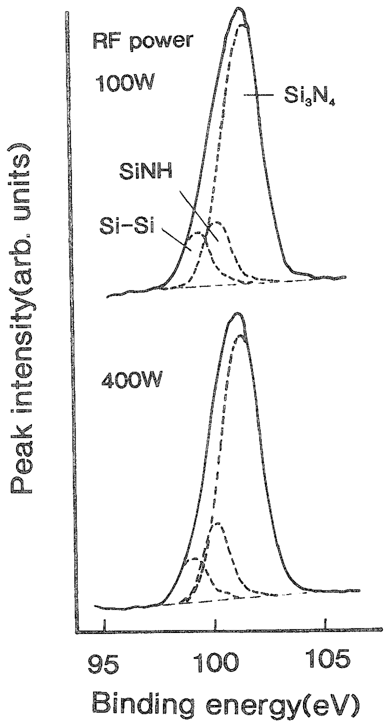
Furthermore, in Fig. 8(b) the result of analysis of SiN_x films deposited by changing the hydrogen ratio or the $H_2/(H_2+N_2)$ ratio shows very little change in the amount of excessive Si–Si bonds, but an increase of SiNH and a decrease of Si_3N_4 when the $H_2/(H_2+N_2)$ ratio increases in the source gas. From these analytical results, it is concluded that constant Si–Si bonds is responsible for the slight decrease in the optical band gap even when the Si/N ratio becomes a Si-rich condition.

Figure 9 shows the relationship between the optical band gap and the spin density determined by ESR. The spin density tends to decrease with the increased optical band gap showing decrease in dangling bonds of silicon. This means that a low content of excessive silicon atoms unbonded with nitrogen atoms exist in the stoichiometric or N-rich SiN_x film which has the high optical band gap, and thus, a low dangling bond density.

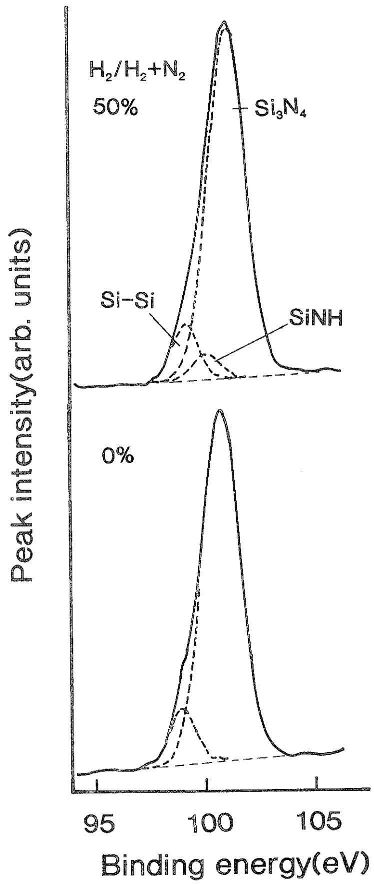
§4. Application to Liquid Crystal Driver TFTs

4.1 *TFT characteristics*

Cracking and an abnormal etching of SiN_x film is often observed when a SiN_x film with higher tensile stress is deposited on a multi-layered device such as TFT. This is caused by an internal stress in the film. Figure 10 shows the SEM photographs of a cross section along a metal line after slightly etching the SiN_x surface with BHF. In contrast to the abnormal etching form at the step of SiN_x



(a)



(b)

Fig. 8. Curve resolved spectra of ESCA for Si 2p in SiN_x deposited under the typical conditions: (a) dependency of RF power, (b) dependency of $H_2/(H_2+N_2)$ ratio.

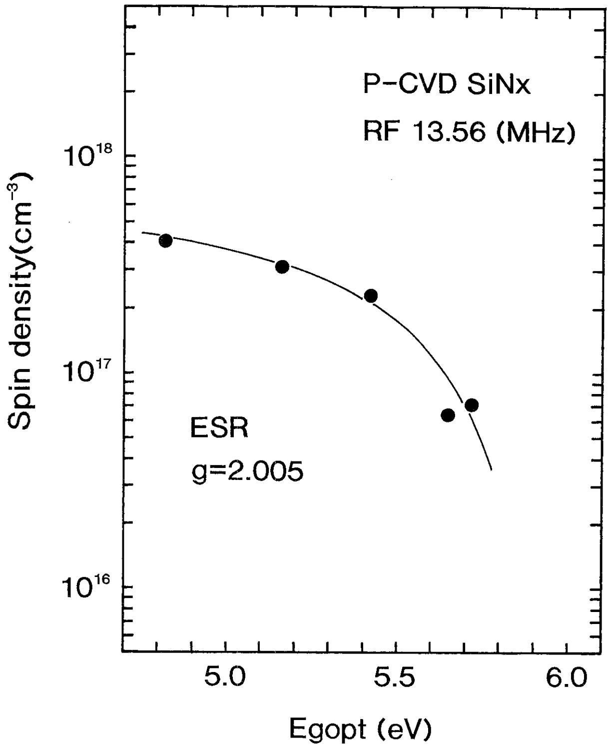


Fig. 9. Si/N atomic ratio as a function of SiN_x optical band gap.

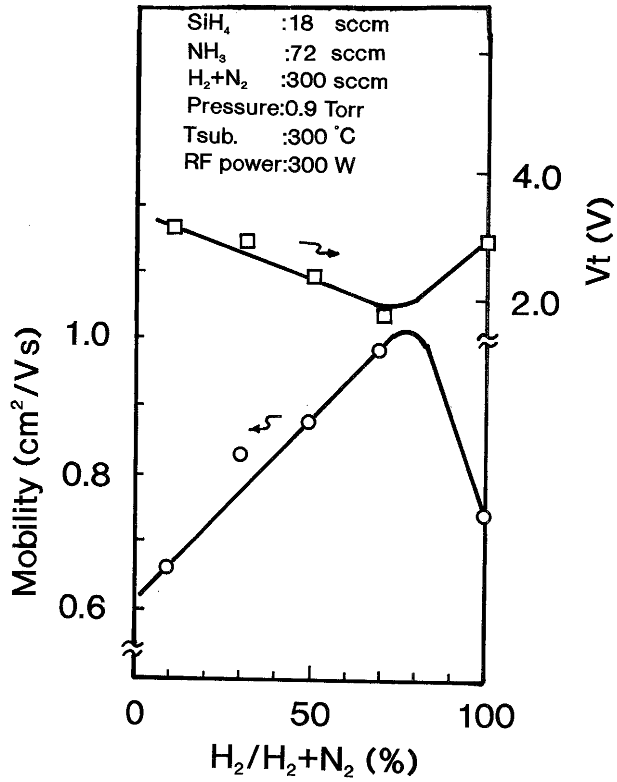
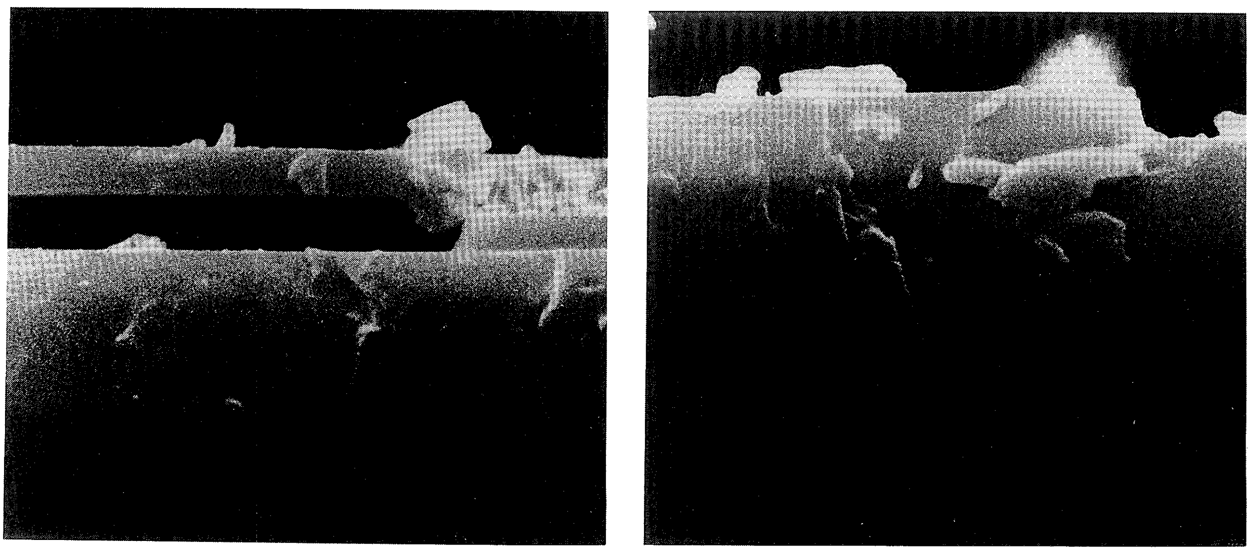


Fig. 11. Effect of the $H_2/(H_2+N_2)$ ratio in the source gas for PECVD SiN_x on mobility and threshold voltage of TFTs.

films showing tensile stresses, the etching form is normal with the films showing compressive stresses, as shown in Figs. 10(a) and 10(b), respectively.

Figure 11 shows the mobilities and threshold voltages (Vt) of TFTs of which gate insulator SiN_x films are prepared by changing the $H_2/(H_2+N_2)$ ratio with the other conditions constant. This shows the best result with TFT using SiN_x film deposited at 70% of the $H_2/(H_2+N_2)$ ratio, or having slight compressive stress. Furthermore, peeling of the a-Si layer in TFT using SiN_x film which is deposited at 100% of the $H_2/(H_2+N_2)$ ratio causes a rapid decrease in mobility and the increase of Vt.[5,6]

This is believed due to a substantial decrease in internal stress at the a-Si/SiN_x interface which causes SiN_x film to be compressive stress since the internal stress of a-Si film is found to be compressive.



(a) (b)

Fig. 10. SEM photographs of cross section along a metal line after slightly etching the SiN_x surface: (a) tensile stress of SiN_x deposited with 0% of $H_2/(H_2+N_2)$ ratio, (b) compressive stress of SiN_x deposited with 100% of $H_2/(H_2+N_2)$ ratio.

4.2 *Reliability*

SiN_x as a gate insulator of TFT is deposited with varied RF powers. The source gas NH_3/SiH_4 ratio is 4 or 6, and $H_2/(H_2+N_2)$ is 30%. Then the optical band gap of SiN_x is varied between 4.8 and 6.0 eV, and the thickness of SiN_x is 400 nm. Figure 12 shows a dependency of threshold voltage shift (ΔVt) on the optical band gap under a constant gate bias stress. The gate bias is 30 V so that the electric field in the SiN_x (E_{SiN}) is 7.5×10^5 V/cm. The ΔVt decreases with increasing optical band gap of the SiN_x film until about 5.4 eV, above which the ΔVt is found to be almost constant.

The Si/N ratio of SiN_x film having a band gap of more than 5.4 eV is either stoichiometric or N-rich, and the reliability of TFT using such a SiN_x film as its gate insulator film is characteristically superior in reliability. SiN_x with a higher optical bandgap shows a decrease of dangling bond density, as described above. Therefore, the substantially decreased density of the trapping state consisting of dangling bonds in SiN_x films causes a decrease in ΔVt.

There have been a few recent studies of the gate insulator composed of double layer of Ta_2O_5 and SiN_x,[7,8] or Al_2O_3 and SiN_x[9] in order to achieve higher production yield and performance of a-Si TFT. We also have measured ΔVt in a-Si TFT with a gate insulator of double layer which are reactively sputtered Ta_2O_5 and SiN_x having the optical band gap of 5.2 eV. The thickness of Ta_2O_5 and SiN_x is both 200 nm. The gate bias stress is set so that the electric field in the SiN of the double layer is equal to that of the single SiN_x layer, through the following equation:

$$Vg_{bias}=E_{SiN}\cdot d_{SiN}\,\frac{d_{TaO}\cdot\varepsilon_{SiN}+d_{SiN}\cdot\varepsilon_{TaO}}{d_{SiN}\cdot\varepsilon_{TaO}}$$

where d_{TaO} and d_{SiN} are thicknesses, and ε_{TaO} and ε_{SiN} are dielectric constant for the Ta_2O_5 and SiN_x films, respectively.

As shown in Fig. 12, ΔVt in a-Si TFT with the double layer is to the same degree as that of the single gate insulator of SiN_x having the optical band gap of 5.2 eV under positive bias stress, while ΔVt with double layer is larger than the predictions for that of the single SiN_x layer under negative bias stress. From these results, it might be thought that under positive bias stress, the mechanism for Vt shift of a-Si TFT with a gate insulator of double layers is the same as that for a gate insulator of sigle layer SiN_x, therefore it is related to the deterioration mechanism at the a-Si/SiN_x interface. On the other hand, under negative bias stress, the Vt shift mechanism of a-Si TFT with a gate insulator of double layers is considered to be different from that of a-Si TFT with a gate insulator of single-layer SiN_x.

Figure 13 shows the time dependence of ΔVt under a

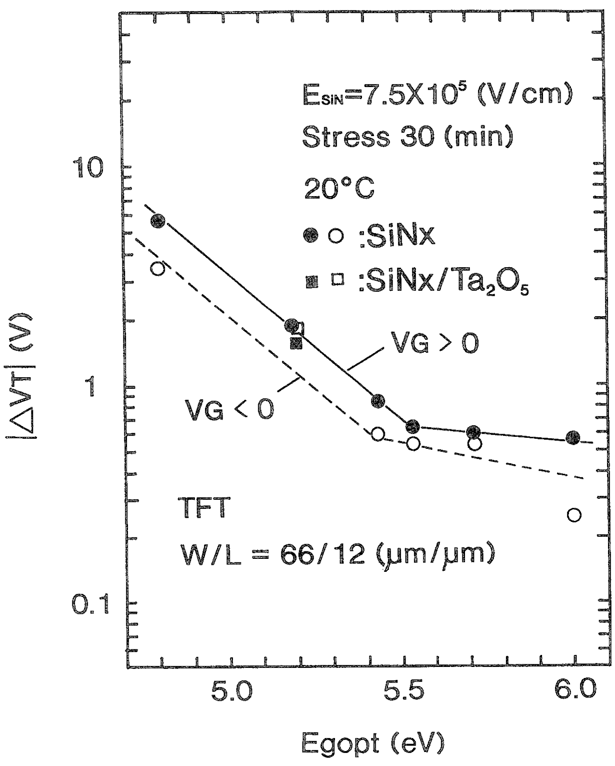


Fig. 12. Threshold voltage shift as a function of SiN_x optical bandgap under positive and negative gate bias stresses.

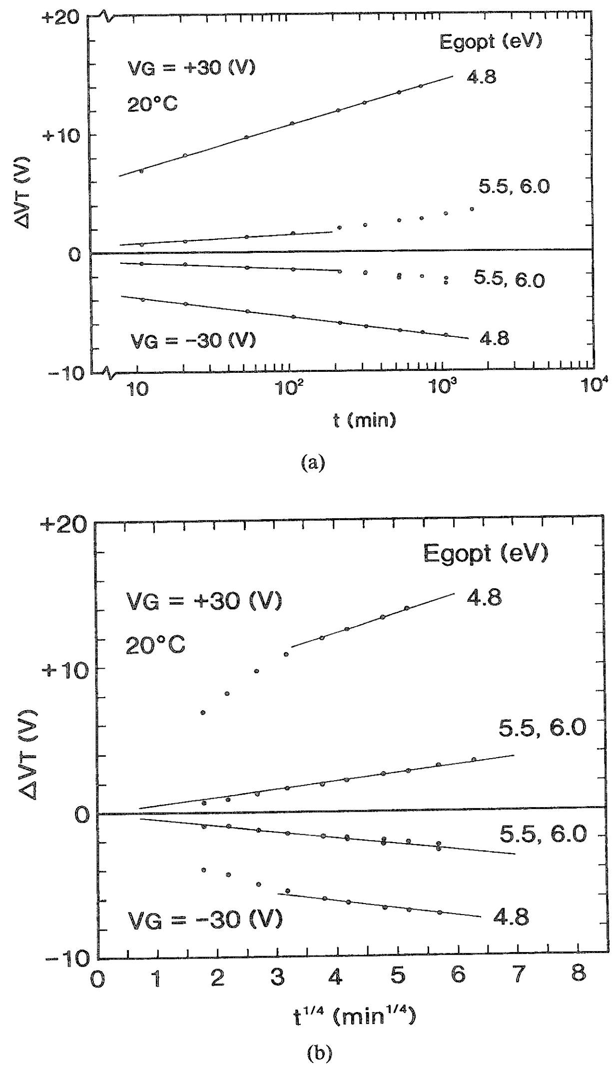


Fig. 13. Time dependence of the threshold voltage shift (ΔVt) for TFTs with different SiN_x optical band gaps. ΔVt is plotted (a) on a linear scale and (b) against $t^{1/4}$.

condition of constant bias. As shown in Fig. 13(a), the change of *Vt* is proportional to log *t* in a short time span or TFT with a gate insulator of a lower optical band gap (4.8 eV), while it is proportional to $t^{1/4}$ in a long time span or TFT with a higher optical band gap (5.5 eV, 6.0 eV), as shown in Fig. 13(b).

These facts suggest two types of deterioration mechanism working on the time dependency of ΔVt. In the first stage of deterioration, ΔVt is believed to be due to the charge trapping in the SiN_x film by modified Fowler-Nordheim tunneling or direct tunneling, and therefore, ΔVt is low for the SiN_x film having a higher optical band gap because of its lower trap density. After the above first stage, the creation of states in a-Si film due to Si–Si bond breaking is responsible for ΔVt.[10–12]

§5. Conclusion

The internal stress of SiN_x film is found to be controllable by changing the ratio of H_2 and N_2 without affecting the optical band gap, and an increase in excessive metallic silicon causes dangling bonds to be produced when it is deposited under a high RF power using a SiH_4, NH_3, N_2 and H_2 system source gas.

Satisfactory TFT characteristics are realized by using a SiN_x film which has either stoichiometric or N-rich composition showing slightly compressive internal stress. In addition, the shift of threshold voltage caused by the charge injection into the traps in gate insulator film is found to directly affect the reliability of TFT in operations of a short time span.

Therefore, it is concluded that TFTs of high reliability can be fabricated by using SiN_x films which have either a stoichiometric or N-rich composition corresponding to the large optical band gap as the TFT gate insulator film.

Furthermore, the characteristics of a-Si are more important to be reliability of TFT in operations of a long time span.

Finally our experimental results suggest that the characteristics of the a-Si/SiN_x interface are very important to the reliability of a-Si TFT with double-layer gate insulators under positive bias stress. The deterioration mechanism under negative bias stress is still to be investigated.

Acknowledgments

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