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Properties of a New Passivation SiN_x Films Prepared by cat-CVD Method

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Silicon nitride thin films (SiN*x* films) are formed at substrate temperatures around 300℃ by the catalytic chemical vapor deposition (cat-CVD) method. In the cat-CVD method, the deposition gases such as a SiH_4 and NH_3 gas mixture are decomposed by the catalytic cracking reactions with a heated tungsten catalyzer placed near the substrate. It is found that the resistivity, breakdown electric field and hydrogen content of the cat-CVD SiN*x* films are almost equivalent to those of high-temperature thermal CVD films, and that the surface diffusion length of depositing species appears large enough to obtain good step-coverage.

1. Introduction

SiN*x* films are used as a passivation film of electronic devices, the gate insulator of thin film transistors (TFT), and also an interlayer insulator in integrated circuits (IC). These all films have to be deposited at low temperatures around 300℃ since devices are already formed before deposition. One of the way of low temperature deposition is plasma CVD (P-CVD) method. However, plasma damage due to the P-CVD process is still a serious problem particularly for compound semiconductor devices such as GaAs IC or light emitting-devices. Additionaly, hydrogen atoms which are contained automatically by more than 10% in P-CVD films sometimes cause device degradation.[1] Thus, the developement of a new deposition technology in which the films with low hydrogen content can be deposited at low temperatures without any plasma has been strongly expected.

One of the authors has developed a new thin-film deposition technique named "catalytic chemical vapor deposition (cat-CVD) method". In the method, deposition gases are decomposed by catalytic cracking reactions with a heated catalyzer placed near substrates, and so that, films are deposited at low temperatures without help from plasma nor photochemical excitation. Actually, the authors have already succeeded to deposite high-quality SiNx thin films by this cat-CVD method using a SiH_4 and N_2H_4 gas mixture.[2]

In this paper, firstly, we show the properties of SiN*x* films prepared by cat-CVD method using a gas mixture of SiH_4 and NH_3. Then we discuss the usefulness of this SiN*x* films as passivation films.

2. Fundamentals for experiment

The deposition apparatus is schematically illustrated in Fig.1. A tungsten wire (diameter is 0.5mm, and total length 130cm) is used as the catalyzer and placed beneath substrates with a distance of 4cm. A catalyzer is coiled, pinned by molybdenum wires and spread widely parallel to the substrate. A thermocouple is mounted just beside the substrates on the substrate holder to determine the substrate temperature (T_s) which includes the effect of thermal radiation from a heated catalyzer. In the present study, T_s is varied from 200℃ to 400℃, but mainly kept at around 300℃. The catalyzer is heated by supplying the electric power directly onto it. The temperature of catalyzer (T_{cat}) is estimated by both a electronic infrared thermometer placed outside of a quartz window and the electric resistivity of catalyzer. The gas pressure (P_g) is measured by both a Pirani vacuum gauge and electronic capacitance manometer, and it is about several mTorr. The flow rate of SiH_4 gas, FR(SiH_4) and that of NH_3 ,FR(NH_3) are 0.5sccm and 0 to 70sccm respectively. This deposition system is much simple and economic compared with conventional P-CVD.

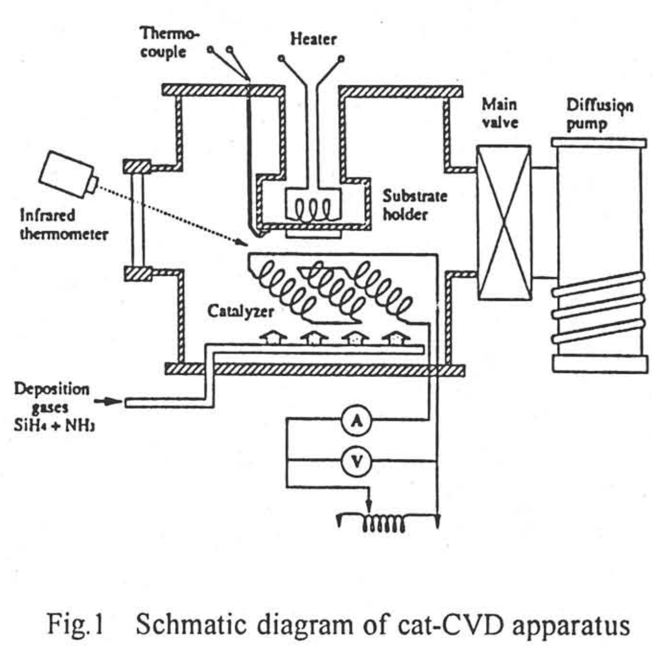

Fig.1 Schmatic diagram of cat-CVD apparatus

3. Results and discussion

3.1 Properties of cat-CVD SiNx film

The atomic composition of the cat-CVD SiNx films is determined by Rutherford backscattering (RBS) measurement using 2.5MeV helium ions. The results are shown in Fig.2. Firstly, catalyzing materials such as tungsten atoms are not observed at all, and it is confirmed that the incorporation of such atoms can be compeletely avoided even though the catalyzer is heated around 1700℃. Secondly, the oxygen is somehow mixed in cat-CVD SiNx films when the flow rate of NH_3 is low, but we can control this mixed oxygen by changing NH_3 flow rate. And it is found that when the flow rate of NH_3 exceeds over 100 times of SiH_4 flow rate, the cat-CVD SiNx films comes to nearly stoichiometric Si_3N_4.

Next, hydrogen content is monitored by infrared (IR) absorption measurement and the results are demonstrated in Fig.3 for the film deposited with $FR(SiH_4)$=0.5sccm, $FR(NH_3)$=50sccm. Absorption peak at about 2000cm^{-1} (Si-H stretching mode) and 3400cm^{-1} (N-H bonds) can not be detected, but only at 515cm^{-1} (Si-H wagging mode) can be seen. According to the formula of Lanford and Rand,[3] hydrogen content of this cat-CVD SiNx film is estimated about 1.5 atomic percent. This low hydrogen content in the cat-CVD films is apparently one of the advantages of using the cat-CVD method.

In Fig.4, the resistivity, the breakdown electric field (B.E.) are summarized as a function of flow rate of NH_3. These were measured by evaporating aluminum electrodes on the SiNx film deposited on a low resistivity Si wafer. When flow rate of NH_3 exceeds over 100 times of SiH_4 flow rate, sufficient insulating properties such as resistivity over 10^{14} Ω cm and breakdown electric field over several MV/cm are realized.

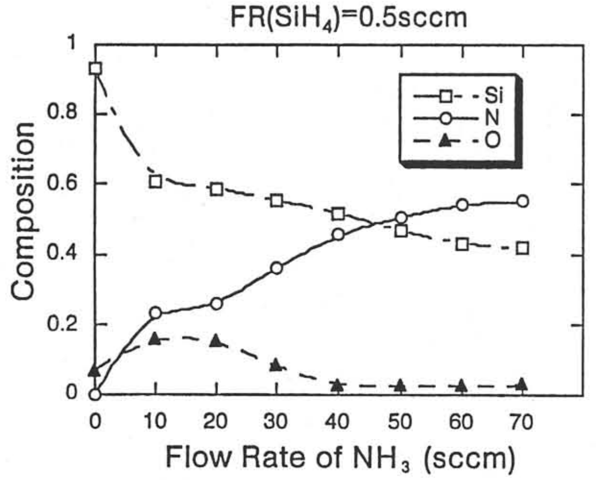

Fig.2 Atomic composition of cat-CVD SiNx films

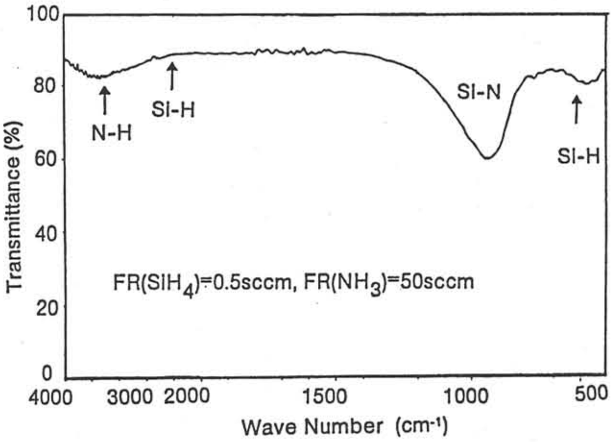

Fig.3 Infrared absorption spectrum

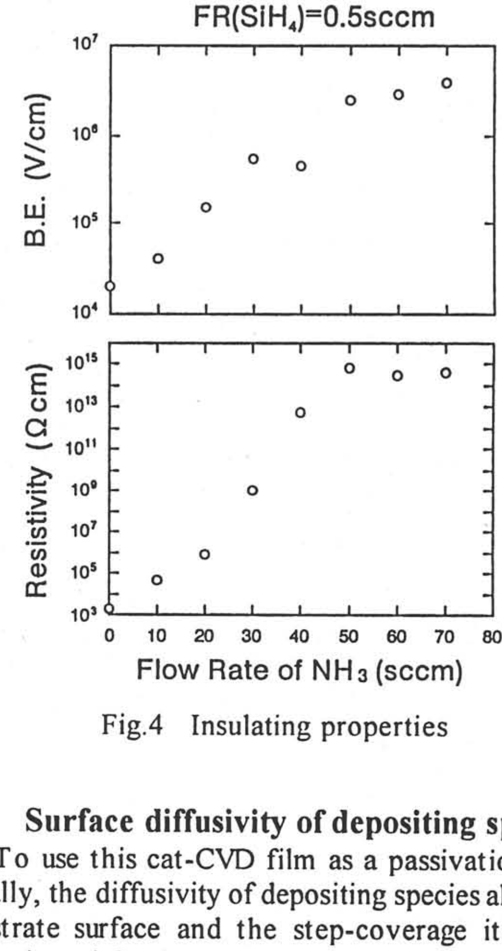

Fig.4 Insulating properties

3.2 Surface diffusivity of depositing species

To use this cat-CVD film as a passivation film, finally, the diffusivity of depositing species along the substrate surface and the step-coverage itself are investigated for the cat-CVD processes. The method for measurement of surface diffusion length (L_D) is schematically illustrated in Fig.5. The diffusivity of species is evaluated by measuring the thickness of SiNx films deposited on the substrate behind the mask, as a function of the distance from the mask edge. The Si mask is fixed above a substrate by a stainless steel spacer with a gap of 20 μm. The film thikness is estimated by using the stylus pressure measurements. The results are shown in Fig.6, taking the substrate temperature as a parameter.

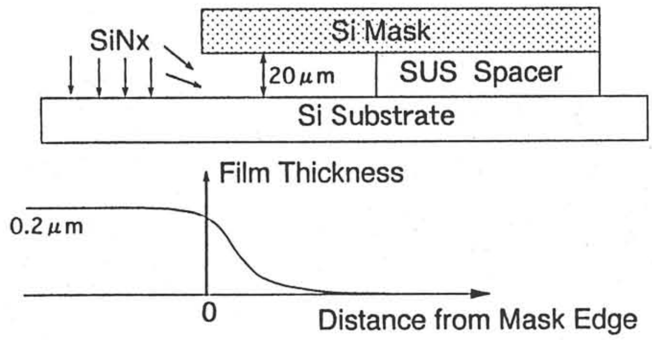

Fig.5 Schematic illustration to measure surface migration of depositing species

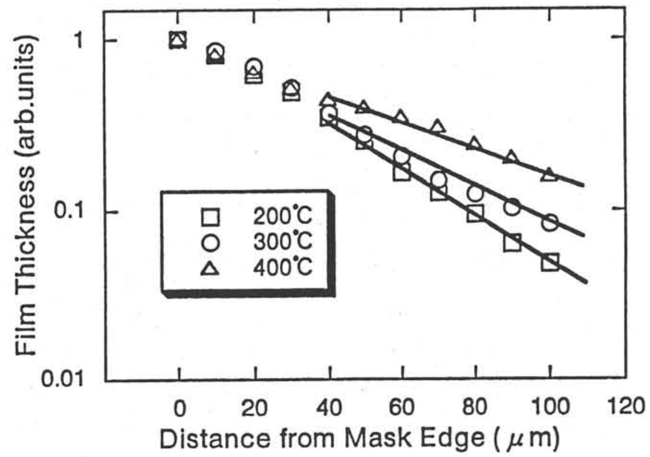

Fig.6 Film thickness of migrated SiNx film

In Fig.6, firstly, it is found that the film can be deposited on the substrate even behind the mask through a narrow gap, and secondly, that film thickness t depends on the distance from the mask edge x by following equation, $t = t_0 \exp(-x / L_D)$. (where t_0 and L_D are constant). In this case, it is suggested that cat-CVD SiNx films within the distance of about 40μm from the mask-edge are formed with depositing species penetrating into the narrow gap in gas phase.On the other hand, for the distance over 40μm, smaller decrease in the distance is observed at higher substrate temperature, and thus, the gradient of these plots are considered equivalent to the surface diffusion length. The diffusion length deposited by Ts=300℃ is about 40μm and has the activation type dependence on the substrate temperatures with the activation energy of about 0.1eV.

From these results, it is suggested that the films can be deposited even on a groove of several tens of μm depth with a good step-coverage by the cat-CVD method, since the migration of species is long enough for any cases.

4. Conclusions

From the studies demonstrated above, the following conclusions are obtained.

1) Stoichiometric SiNx films can be obtained at around 300℃ by the cat-CVD method when flow rate of NH_3 exceeds over 100 times of SiH_4 flow rate.
2) Hydrogen content in the cat-CVD films is much lower than that in P-CVD films, and only a few atomic percent.
3) The cat-CVD SiNx films have sufficient insulating properties, such as resistivity over 10^{14} Ω cm and breakdown electric field over several MV/cm are easily obtained.
4) Surface diffusion length of depositing species is about several-tens of μm and appears long enough to realize good step-coverage.

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References

1) Pierre boher, Monique Renaud, L.J. vanljzendoorn, and Yves Hily, Appl. Phys. Lett. **54** (1989) 511.
2) H.Matsumura, Japan. J. Appl. Phys. **28** (1989) 2157.
3) W. A. Lanford and M.J.Rand, J. Appl. Phys. **49** (1978) 2473