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MOS DEVICES.

DISTRIBUTION AND ROLE OF N—H
AND Si—H BONDS IN MNOS STRUCTURES

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Résumé. — Nous avons étudié les effets de traitement thermique à haute température sur les qualités structurales et électriques des structures de mémoire MNOS en utilisant la spectroscopie MIR pour déterminer les liaisons N—H et Si—H. Les méthodes électriques étaient les suivantes : temps de rétention, l'analyse de la courbe d'hystérésis de mémoire, la technique C-V et TSC. Les résultats montrent qu'il y a un rôle considérable de la température du traitement thermique dans les variations des liaisons N—H et Si—H. Nous avons trouvé le plus grand changement dans le nombre des liaisons Si—H et N—H au voisinage de l'interface $\text{SiO}_2\text{-Si}_3\text{N}_4$. On a trouvé un accord entre la charge fixe à l'interface, la durée de rétention de charge avec le changement du nombre de liaisons Si—H et N—H. Les données électriques ont montré une forte dépendance entre la température et la durée du traitement thermique, sur le gaz utilisé pour le traitement aussi. Les courbes TSC étaient considérablement différentes pour les MNOS structures traitées que pour celles non traitées.

Abstract. — The effects of high temperature annealing on the structural and electrical properties of MNOS memory structures have been studied using multiple internal reflection (MIR) spectroscopy to determine the N—H and Si—H bonds in Si_3N_4 layer. Electrical methods applied were : the memory window decay rate, analysis of memory hysteresis, C-V curves and TSC technique. Results showed that there is an important role of the annealing temperature in the change of N—H and Si—H bonds. We have found the largest change in the number of N—H and Si—H bonds in the vicinity of $\text{SiO}_2\text{-Si}_3\text{N}_4$ interface. The change of fixed charge at the $\text{SiO}_2\text{-Si}_3\text{N}_4$ interface, the retention time and width of memory window are closely related to the change in the number of the Si—H and N—H groups. Electrical data showed a strong dependence not only on annealing temperature and time but on the composition of gas atmosphere used during the annealing. The TSC curves were significantly different for the annealed and unannealed MNOS structures.

1. Introduction. — The Si_3N_4 films deposited by CVD method are technologically important components of the nonvolatile MNOS (metal- $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Si}$) elements. Therefore a lot of papers have dealt with both the structural [1-5] and the electrical [6, 7] properties of the CVD Si_3N_4 films.

It was shown in the works of Stein *et al.* [2-5] that Si_3N_4 films deposited by the reaction of SiH_4 and NH_3 contain H atoms chemically bound to N and Si (N—H and Si—H groups respectively). They supposed that these groups could play substantial role in the electrical properties of Si_3N_4 films and MNOS transistors. Therefore the foregoing authors have measured the optical densities corresponding to the peaks of N—H and Si—H infrared absorption bands respectively as a function of etch time (film thickness) [4].

On the other hand Neugebauer [6] and Kasprzak [7] have concluded on the base of their measurements, that the memory window decay rate of MNOS memory devices is connected with the depth distribution of charges in the Si_3N_4 films.

Bélyi *et al.* [1] have demonstrated the influence of the composition of the ambient gas on decomposition of N—H groups during annealing at 1 000 °C.

In the present work we have studied the distribution

of Si—H and N—H bonds in the Si_3N_4 layer and the connection between the change of H content and some important electrical parameters of the MNOS structures.

2. Experimental details. — The depth distribution of N—H and Si—H groups in the Si_3N_4 films has been measured by means of multiple internal reflection (MIR) spectroscopy. The Si_3N_4 films were deposited on both sides of 195 $\Omega\text{ cm n}$ type thermally oxidized MIR plates of $1.7 \times 10 \times 0.5\text{ mm}^3$ dimension with 45° end faces. Thickness of the thin SiO_2 films was 2.2 nm. The geometry and the dimensions of the plate used in present investigation gave 34 internal reflections at the film-covered surfaces. The Si wafers for electrical measurements were 1.5 $\Omega\text{ cm n}$ type (111).

The deposition processes were carried out at 1 : 75 ratio of SiH_4 and NH_3 , the carrier gas was nitrogen or mixture of 5 % H_2 and 95 % N_2 . The Si_3N_4 films were etched off step by step in HF and NH_4F buffer at 70 °C and the MIR spectra of the films were measured at every film thickness by Zeiss UR 10 double beam spectrophotometer equipped with MIR attachment and a bare Si sample in the reference beam for compensation.

The absorption coefficients of N—H and Si—H groups were calculated using the thin film approximation [11]. The thickness and the refractive index of the film were measured by Gaertner L 119 ellipsometer. The electrical contacts to the nitride on Si wafer were prepared by vapor depositing Al dots onto the film.

The electric measurements carried out on the MNOS structures were :

1. Analysis of C-V curves to determine the charge distribution in the vicinity of the SiO_2 - Si_3N_4 interface.
2. Measurement of thermally stimulated currents (TSC) to investigate the charge trapping.
3. The memory window decay rate measurement to characterize the charge retention.

3. Results and discussion. — In the first group of our experiments the depth distribution of N—H and Si—H groups in the Si_3N_4 films and the effect of deposition temperature and annealing were examined. The α absorption coefficient (measured at $3\,255\text{ cm}^{-1}$ wave number) related to the N—H groups [8] as a function of film thickness (d) is shown in figure 1.

FIG. 1. — The NH peak absorption coefficient (α , at $3\,255\text{ cm}^{-1}$) as a function of film thickness (d) for Si_3N_4 deposited onto SiO_2 layer of 2.2 nm thickness thermally grown onto Si MIR plate.

It can be seen that the α is almost constant in the thickness interval of 40-50 nm from Si_3N_4 -air interface. Decreasing the film thickness below 100 nm at first changes in the concentration of N—H bonds are seen, with a final sharp increase approaching the SiO_2 - Si_3N_4 interface. This is contrary to the results of Stein [4] who found that the N—H concentration is constant along the thickness of the Si_3N_4 films. However, the annealing process resulted in a considerable decrease in the number of N—H groups at this interface. The α absorption coefficient (measured at $2\,246\text{ cm}^{-1}$ wave number) corresponding to the Si—H groups [8-10] is plotted against the film thickness in figure 2.

Qualitatively the course of the $\alpha(d)$ depth distribution of Si—H groups is similar to that of the N—H

FIG. 2. — The SiH peak absorption coefficient (α , at $2\,246\text{ cm}^{-1}$) as a function of film thickness (d) for Si_3N_4 deposited onto SiO_2 layer of 2.2 nm thickness thermally grown onto Si MIR plate.

groups. It is remarkable that our Si_3N_4 films contained Si—H groups even at depositions at 950°C though according to the experiments of Stein and co-workers [4], Si_3N_4 film prepared at temperatures higher than 900°C do not contain observable quantity of Si—H groups. This difference can be explained by the condition of deposition carried out in hydrogen containing atmosphere, which hindered the escape of the H atoms from the film. So it looks probable that not only the deposition temperature but the hydrogen content of the carrier gas play a role in the presence of Si—H bonds.

Following the determination of depth distribution of N—H and Si—H groups C-V curves were measured as a function of film thickness. The result of this analysis is shown in figure 3 where the flatband voltage is plotted against the film thickness. There is a considerable difference between the annealed and unannealed films. The initial flatband voltage of the annealed film is significantly lower. An oscillation of

FIG. 3. — The flatband voltage as a function of film thickness.

charges at the distance 30 nm from the $\text{SiO}_2\text{-Si}_3\text{N}_4$ interface is shown in the annealed film; the positive and negative value of the second derivative represents positive and negative local charges, resp.

Information was obtained on the trap conditions of Si_3N_4 films before and after annealing by measurement of thermally stimulated currents. The heat treatment caused considerable changes in TSC curves, as it is shown in figure 4. Probably the trap concentration is higher in the annealed film than it was before annealing.

FIG. 4. — TSC curves for MNOS structures before (2) and after (1) annealing (t_w is the write time; V_w write in voltage; V_m read out voltage).

The initial fixed charge obtained by the analysis of the C-V curves and the memory window decay rate are important parameters, characterizing MNOS memory devices.

The normalized decay rate [12] and the integrated charge as a function of annealing temperature at two different ambient gas are shown in figure 5. It can be

FIG. 5. — The normalized decay rate (a) and the integrated charge (b) as a function of the annealing temperature.

seen that the normalized decay rate and the integrated charge are decreasing with increasing annealing temperature. This means, that MNOS memory transistors made using annealed Si_3N_4 films have a smaller memory decay rate.

Comparing the effect of annealing on the depth distribution of N—H (Fig. 1) and Si—H (Fig. 2) groups and on the normalized decay rate (Fig. 5), we can see that the decreased hydrogen content near the $\text{SiO}_2\text{-Si}_3\text{N}_4$ interface has a favourable effect on the decay rate. This is in accordance with the result that values of normalized decay rate are smaller if annealing was carried out in pure nitrogen gas. These observations are in agreement with the experiments of Belyi [1] who found that the decomposition rate of N—H bonds depends on the hydrogen content of the ambient gas used in the annealing process.

Further information on the effect of the Si—H and N—H groups on normalized decay rate and integrated charge can be obtained by measuring the foregoing characteristics as a function of annealing time. In figure 6 is shown the dependence of normalized decay rate and integrated charge on the time of heat treatment. The normalized decay rate has a maximum and integrated charge has a minimum after annealing, at 900 °C in forming gas for 10 min. This phenomenon can be interpreted using the suggestion of Stein [3, 5], namely the increase of normalized decay rate after 10 min annealing is caused by the increasing number of the Si—H groups, being created by transfer of H from N—H bonds to the uncompletely bounded Si.

FIG. 6. — The normalized decay rate (a) and the integrated charge (b) as a function of annealing time.

Stein's [3] results are presented in figure 7. The local maximum of Si—H absorption occurs after about 10 min. of annealing.

FIG. 7. — The optical density relating to SiH and NH groups as a function of annealing time according to Stein *et al.* [3].

In our case we have got the local maximum of normalized decay rate at 900 °C after 10 min. of annealing in forming gas. This difference can be explained again by the H content of the forming gas.

If the annealing is carried out in nitrogen at 900 °C no maximum can be seen.

4. Summary. — The depth distribution of N—H and Si—H groups in the Si_3N_4 films has been determined, and electric parameters of these films being important from the point of view of their function in MNOS memory cells have been measured. We can summarize our experiences in the following conclusions :

1. The concentration curves of SiH and NH groups, resp. are changing rather steeply in the vicinity of SiO_2 - Si_3N_4 interface in comparison with their distribution inside the film.

2. Annealing or changing the deposition temperature influence these concentration distributions mainly in the vicinity of the SiO_2 - Si_3N_4 interface.

3. The change in the H content of the heat treated films depends not only on the annealing temperature and time but also on the H content of the annealing ambient gas.

4. Important electrical parameters (flatband voltage, width of memory window, normalized decay rate) of MNOS memory cells depend upon the concentration distribution of Si—H and N—H groups in the film.

5. Both annealing 10-15 min at 900 °C in nitrogen and that of 15 min at 1 000 °C in forming gas produces MNOS structures with advantageous electrical parameters.

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