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HYDROGEN DISTRIBUTION IN OXYNITRIDE / OXIDE STRUCTURES

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Silicon oxynitride films with five different O/N ratios were deposited with low pressure chemical vapor deposition on a silicon substrate covered with an oxide. The films were subjected to subsequent post-deposition anneals in N_2 and H_2 at 1000 °C, and a H plasma at 300 °C to obtain information about the hydrogen chemistry. The overall film compositions were determined with elastic recoil detection. The resonant reaction $^{15}N(^{1}H, \alpha\gamma)^{12}C$ was used to obtain hydrogen depth profiles. The hydrogen depth profiles are characterized by a value for the bulk concentration and width of the interfacial region. We found that the stability of the hydrogen in the bulk has a maximum for $O/N \approx 0.32$. From the measured interfacial widths we deduced that for low values of O/N the stability of hydrogen in the interfacial region is relatively large. For intermediate values of O/N the stability of the hydrogen in the bulk and the interfacial region do not differ significantly, while for high O/N a relatively low stability of the interfacial hydrogen is observed. The O/N dependence of the stability of the interfacial hydrogen is consistent with the bulk stability if we assume that the interfacial oxynitride is oxygen enriched as compared to the bulk oxygen concentration.

1. Introduction

Thin silicon nitride (Si_3N_4) films are widely used as dielectric in metal nitride oxide semiconductor (MNOS) structures for non-volatile memories. In a memory device the electrical performance of the nitride and its interfaces is very important. Charge trapping characteristics of the materials and memory retention time are usually associated with Si–H and N–H bonding configurations. The presence of hydrogen in the material could reduce the number of potential trapping sites, which would increase the memory retention time [1–3].

It has been reported that charge transport in MNOS structures can be reduced by replacing the Si_3N_4 film by a silicon oxynitride (SiO_xN_y) film [4]. We believe that the origin for this reduction can be found in the hydrogen distribution of oxynitride film. In a previous paper some of the authors reported on the annealing of oxynitride in a 7% H_2/N_2 ambient at 1000 °C

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[5]. In this paper we will report on the hydrogen distribution after subsequent annealing of oxynitrides in flowing N_2 and H_2.

Hydrogen profiles have been measured using the resonant nuclear reaction $^1H(^{15}N, \alpha\gamma)^{12}C$ (NRA). Special attention was paid to the oxynitride/oxide/silicon interface, since the charge trapping occurs in that interfacial region.

2. Experimental

Samples were deposited at IMEC, Leuven, Belgium with low pressure chemical vapor deposition (LPCVD) from a mixture of 25 sccm SiH_2Cl_2 and 75 sccm $NH_3 + N_2O$ at 800–820 °C. Oxynitrides with five O/N ratios were obtained by varying the NH_3/N_2O ratio. Samples were deposited on a silicon substrate with a native oxide, or a thin or thick thermal oxide.

After deposition samples were subsequently annealed in N_2 (3.6 ℓ/min) for 1 h at 1000 °C, H_2 (85 ℓ/min) for 1 h at 1000 °C and a H plasma for 1 h at 300 °C. The H plasma was produced with 300 W RF power (13.56 MHz) in a H_2 flow of 100 sccm with a pressure of 123 mTorr.

The 60 samples resulting were analyzed with elastic recoil detection (ERD) for the O/N ratio and nuclear reaction analysis (NRA).

For the ERD measurements a 30 MeV ^{28}Si beam was used. More details can be found in ref. [6].

The resonant nuclear reaction $^1H(^{15}N, \alpha\gamma)^{12}C$ was used to obtain depth profiles of hydrogen in the samples. The γ-yields were converted into hydrogen concentrations by comparison with the yield of a standard (a LPCVD Si_3N_4 film).

3. Data reduction

3.1. The composition of the samples

In ERD the number of recoiled particles detected (P) is proportional to the recoil cross section (σ) and the concentration in the film (N). Therefore the O/N ratio in the oxynitride can be calculated as

$$O/N = P_O\sigma_N / P_N\sigma_O. \tag{1}$$

For the analysis of the spectra we had to separate the contributions of oxygen in the oxynitride and oxygen in the underlying oxide. In the oxynitrides with a thick thermal oxide, the transition from oxygen in the oxynitride to oxygen in the oxide can be distinguished in the recoil spectra. This is not the case for samples with a native or thin thermal oxide. For these samples we corrected the yield for the oxygen using the values found for the as-deposited nitrided samples.

3.2. The hydrogen depth distribution

The γ-yield at a certain beam energy E_b can be written as

$$N_t(E_b) = C \int \frac{N_H(x)}{\sigma(x)} \exp\left\{ -\frac{[E_b - E_r - S(x)]^2}{2\sigma^2(x)} \right\} dx, \tag{2}$$

in which x is the depth in the sample, $N_H(x)$ the hydrogen depth distribution, E_r the resonance energy of the reaction and $S(x)$ the total energy loss due to stopping. If the hydrogen distribution is constant over the film thickness, $N_t(E_b)$ at the interface (at a depth d) can be approximated with an integrated gaussian distribution function with a mean value $E_r + S(d)$, a width σ_i and a height H which is proportional to the hydrogen bulk concentration (fig. 1).

Two methods have been used to characterize the measured yield curves:

- numerical integration of eq. (2) and changing $N_H(x)$ until a satisfactory agreement between calculated and measured γ-yield is found;
- fitting an integrated gaussian function to the measurement.

Comparison of the results obtained with both these methods showed that a pile-up of hydrogen near the interface with the substrate results in a decrease of σ_i and vice versa. This is due to the limited depth resolution. Therefore σ_i must contain a component σ_{act} describing the width of the interfacial region in which the hydrogen concentration diminishes, the actual interface width. According to Geissel et al. [7] the range straggling contribution to σ_i is proportional to the total energy loss ΔE due to stopping. We used the formula as proposed by Habraken et al. [5]:

$$\sigma_{act}^2 = \sigma_i^2 - \sigma_b^2 - A\,\Delta E, \tag{3}$$

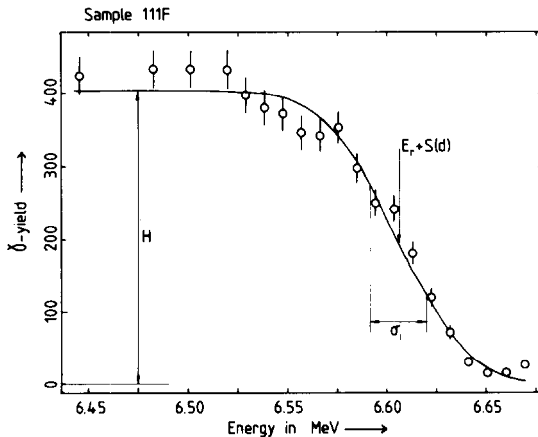

Fig. 1. Hydrogen depth profile measured with NRA. The parameters used to fit an integrated gaussian distribution function are indicated.

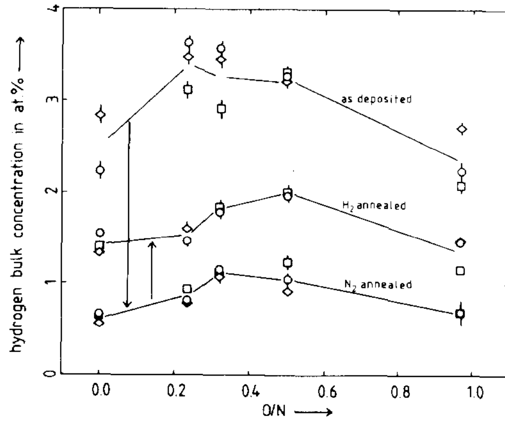

Fig. 2. Hydrogen bulk concentration in as-deposited samples and samples after subsequent N_2 and H_2 annealing. For explanation of the symbols used, see insert in fig. 3.

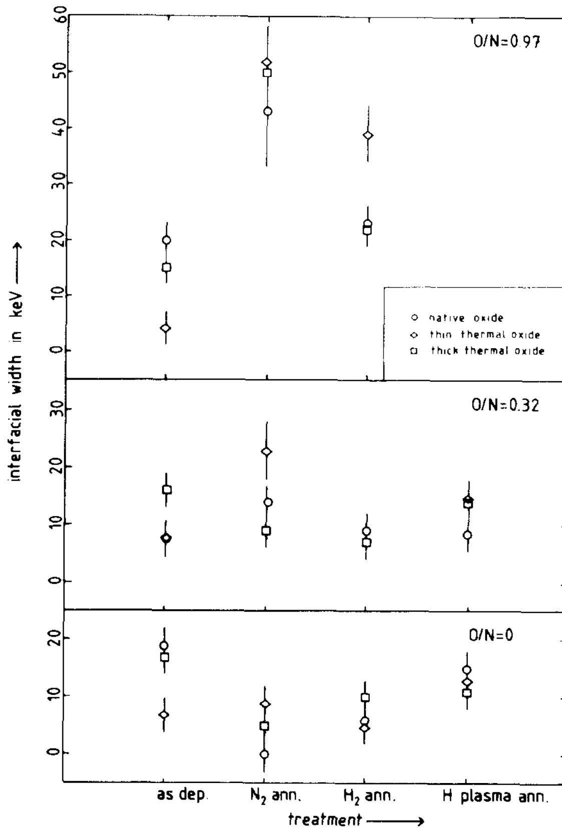

Fig. 3. Actual interface width in as-deposited samples and samples after subsequent N_2 and H_2 annealing.

with σ_b the energy width of the particle beam. For silicon nitride A was determined to be 0.84 ± 0.09 [5]. In this work we will assume this value of A to be independent of O/N.

4. Results

The hydrogen bulk concentration $[H]_{bulk}$ as determined from NRA measurements is given in fig. 2 as a function of the sample composition O/N. It shows a maximum for $O/N \approx 0.3$. $[H]_{bulk}$ decreases during N_2 annealing and increases again during H_2 annealing, although it remains below the initial value. The $[H]_{bulk}$ maximum shifts to a higher O/N ratio after successive anneal steps.

The behaviour of the interface width, determined by NRA shows a clear dependence on both sample composition and annealing treatment. It is indicated in fig. 3. For low values of O/N σ_{act} has a minimum after N_2 anneal. For high values of O/N a maximum is observed after N_2 annealing (fig. 3).

In all plasma annealed samples a high hydrogen concentration is observed in the topmost layer (about 100 Å thick). In the plasma annealed samples with $O/N \approx 0.97$ and an underlying thin or thick oxide, a hydrogen concentration of about 7% in the oxide is found.

5. Discussion

In order to obtain samples with a high O/N value N_2O is substituted for NH_3. As N_2O is less reactive than NH_3 [8], the N_2O/NH_3 ratio must be increased more than proportional to the desired O/N ratio. Thus the supply of hydrogen is strongly reduced when films with a high O/N ratio are grown. Habraken et al. [8] nevertheless observed a constant hydrogen concentration of 3 at% up to $O/N = 0.4$. In our measurements we even observed an increase of the hydrogen concentration up to $O/N \approx 0.3$.

This increase of the hydrogen bulk concentration with O/N may be explained as follows. In silicon oxynitrides only N–H and Si–H bonds are observed in considerable numbers, whereas no O–H bonds are observed. This is concluded from infrared measurements [9]. The concentration of silicon and nitrogen decreases with increasing O/N, so less potential sites for H bond formation are available, but the strength of Si–H and N–H bonds may increase with O/N due to the greater electronegativity of oxygen, as suggested in the literature [9].

With infrared measurements Remmerie [9] found that hydrogen is bound to nitrogen in an amount of approximately 2 at%, independent of O/N. There-

fore changes of the hydrogen bulk concentration must be ascribed to changes in the Si–H concentration.

Next we will discuss the influence of the different annealing treatments on the hydrogen concentration. Since hydrogen loss during annealing is determined by the bond strength [10], we assume that the decrease of the hydrogen concentration during N_2 annealing reflects the strength of the hydrogen bonds.

During N_2 annealing the relative decrease of the hydrogen concentration is the lowest for $O/N \approx 0.4$, so its stability has a maximum for this value of O/N.

During the H_2 annealing the hydrogen concentration increases again, but remains below the value observed for as-deposited samples. It appears that the release of hydrogen from the oxynitride is only partly reversible. To explain this partial reversibility, we note that the release of bound hydrogen during the N_2 anneal may be partly due to cross-linking [11]

$$\text{Si–H} + \text{N–H} \rightarrow \text{Si–N} + H_2. \qquad (4)$$

We notice that since N–H is present in over-abundance, the amount of Si–H will limit the rate of cross-linking.

The as-deposited oxynitrides have a abrupt interface with the substrate. For low O/N σ_{act} decreases after N_2 annealing, so more hydrogen is remaining in the interfacial region than in the bulk, indicating that hydrogen is relatively strongly bound near the interface. For high values of O/N the opposite effect is observed. No difference between the hydrogen in the bulk and the interfacial region is observed for intermediate values of O/N.

From the measurements presented in this paper, we can deduce that the hydrogen stability increases with O/N for low values of O/N and decreases with O/N for high values of O/N. The maximum stability occurs for $O/N \approx 0.4$. The observed behaviour of the hydrogen in the interfacial layer is consistent with the observed O/N dependence of the hydrogen stability in the bulk, if we assume that the interfacial region in the (oxy)nitride in more oxygen-rich than the bulk of the film. Indeed, in LPCVD Si_3N_4 such an increase of the interfacial oxygen concentration has been observed in a layer of 3–4 nm thickness near the interface [12].

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References

[1] J.A. Topich and R.A. Turi, Appl. Phys. Letters 41 (1982) 641.
[2] H.E. Maes and J. Remmerie, in: Proc. Symp. on Silicon Nitride Thin Insulating Films, Electrochem. Soc. Meeting, San Fransisco, CA, May 1983, p. 73.
[3] J. Robertson and M.J. Powell, Appl. Phys. Letters 44 (1984) 415.
[4] A.E.T. Kuiper, S.W. Koo, F.H.P.M. Habraken and Y. Tamminga, J. Vacuum Sci. Technol. 20 (1983) 62.
[5] F.H.P.M. Habraken, J.B. Oude Elferink, P. Eppenga and A.E.T. Kuiper, in: Proc. Three Day In-Depth Review in the Nuclear Accelerator Impact in the Interdisciplinary Field, Padua, 1984, p. 50.
[6] J.B. Oude Elferink, K. Dunselman, E.J. Evers, F.H.P.M. Habraken, W.F. van der Weg and J. Holsbrink, Surface Interface Anal. 9 (1986) 293.
[7] H. Geissel, Y. Laichter, W.F.W. Schneider and P. Armbruster, Nucl. Instr. Methods 215 (1983) 329.
[8] F.H.P.M. Habraken, R.H.G. Tijhaar, W.F. van der Weg, A.E.T. Kuiper and M.F.C. Willemsen, J. Appl. Phys. 59 (1986) 447.
[9] J. Remmerie, Thesis, University of Leuven (1987).
[10] H.J. Stein and H.A.R. Wegener, J. Electrochem. Soc. 124 (1977) 908.
[11] C.M.M. Denisse, K.Z. Troost, F.H.P.M. Habraken, W.F. van der Weg and M. Hendriks, J. Appl. Phys. 60 (1986) 2543.
[12] J.A. Wurzbach and F.J. Grunthaner, J. Electrochem. Soc. 130 (1983) 691.