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NON VOLATILE MEMORY STRUCTURES.

HIGH-TEMPERATURE HYDROGEN ANNEAL OF MNOS STRUCTURES

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Résumé. — Cet article traite l'évolution de la densité d'états d'interface au cours de recuits à hautes températures en hydrogène par des fenêtres dans la couche de nitrure de silicium à proximité des régions MNOS actives. On observe une influence apparente de la géométrie des structures MNOS en conséquence du mécanisme de diffusion latérale de l'hydrogène. En dehors de cette diffusion latérale on observe également une diffusion verticale de l'hydrogène à travers la couche de nitrure à des températures au-delà de 850 °C.

Abstract. — The effects on fast surface state density due to high-temperature hydrogen anneals through windows in the silicon nitride layer next to the active MNOS regions are presented. A marked geometry effect is observed as a result of the occurring lateral hydrogen diffusion mechanism. Besides this lateral diffusion process, a vertical hydrogen diffusion through the nitride layer is observed at temperatures above 850 °C.

1. Introduction. — It is well known that the density of fast surface states, located at the SiO_2 -Si interface of thermally oxidized silicon structures is reduced during the low-temperature (400-500 °C) aluminum sintering step in nitrogen or forming gas (10 % H_2 , 90 % N_2).

In order to test Balk's hypothesis [1] that some hydrogen form is responsible for the reduction of fast surface state density, Castro and Deal [2] annealed MOS structures in 100 % hydrogen. They found that a low-temperature treatment (400-500 °C) in a hydrogen ambient is almost as effective in reducing the density of fast surface states as the aluminum sintering step.

In the case of MNOS structures, however, it has been reported by Deal, MacKenna and Castro [3] that the very dense structure of the silicon nitride layer prevents or at least retards the diffusion of hydrogen through the nitride layer during the aluminum sintering step, so that little or no reduction of fast surface state density is observed.

However, if the silicon nitride is removed in the vicinity of the active MNOS regions, it is possible to reduce the number of fast surface states by means of a heat treatment in 100 % hydrogen. In that case, the hydrogen diffuses vertically through the windows in the nitride layer and migrates then horizontally into the active MNOS regions to the SiO_2 -Si interface, where it annihilates the fast surface states.

In the case of MOS structures the hydrogen has only to diffuse through an oxide thickness of 1 000 to 2 000 Å to reach the SiO_2 -Si interface. For MNOS structures, where the hydrogen has to diffuse from outside the active regions, through the cutouts in the silicon nitride layer, the diffusion length, in order to reach the SiO_2 -Si interface at the center of the structure, is considerably larger, typically 100 to

1 000 times larger. Therefore, if, in the case of MNOS structures, the anneal temperature is increased, not only will the available amount of active hydrogen in the annealing ambient be larger, but also will the diffusion coefficient of the hydrogen increase, so that the lateral hydrogen diffusion into the active MNOS regions will be accelerated.

A program is carried out to study the influence of high-temperature hydrogen anneal on the number of fast surface states at the SiO_2 -Si interface. The results of these experiments are summarized in this paper.

2. Experimental. — **2.1 PROCESSING.** — All silicon used as starting material for this work is n-type with a concentration of $1.1 \times 10^{15} \text{ cm}^{-3}$. Crystal orientation is (100).

The different technological steps involved are presented in figure 1. After a standard cleaning procedure the wafers are thermally oxidized to give an oxide thickness of approximately 1 μm (Fig. 1a). Using conventional photoresist and etching techniques, the active MNOS regions are defined (Fig. 1b). A thin oxide is then thermally grown in dry oxygen for 30 min., at 780 °C, followed by a silicon nitride deposition for 7 min. at 800 °C using the silane-ammonia reaction (Fig. 1c). The ellipsometrically measured thicknesses of the thin oxide and the silicon nitride layers are respectively 50 Å and 770 Å.

The silicon nitride is removed next to the active regions (Fig. 1d). In a subsequent heat treatment in 100 % H_2 , the hydrogen diffuses vertically through these cutouts and migrates then horizontally into the active regions where it annihilates the fast surface states. Cooling after annealing is also in hydrogen, in order to prevent the out-diffusion of hydrogen and/or the introduction of new fast surface states when cooling in nitrogen.

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FIG. 1. — Preparation of hydrogen-annealed MNOS structures.

Filament evaporation of the aluminum (Fig. 1e) is employed to avoid radiation-induced traps in the oxide, which are characteristic of electron-beam evaporation. After the metallization pattern definition (Fig. 1f), aluminum is also evaporated on the back side to ensure a good ohmic contact.

The final low-temperature sintering step is carried out at 450 °C for 30 min in forming gas.

2.2 EVALUATION. — The fast surface state density N_{ss} is measured using the quasistatic low-frequency C-V technique of Kuhn [4] and Castagné [5]. The current response of the MNOS capacitor on a linear voltage ramp is measured with an operational amplifier to plot the C-V curve directly. With this method it is very difficult to determine the density N_{ss} with an accuracy better than $1.0 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$.

3. Results. — In order to find out for which temperature and time the hydrogen anneal is most effective in reducing the fast surface state density, different MNOS structures are processed which have the same history prior to and after the high-temperature hydrogen anneal. Only the anneal conditions are different.

As a reference for the measurements on the annealed structures, a N_{ss} -value of $3.1 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ is used, which is measured on not-annealed MNOS structures with an otherwise completely identical processing history as the annealed samples.

3.1 ANNEAL TEMPERATURE EFFECTS. — The effect of anneal temperature in the 750-1 050 °C range on

the fast surface state density is shown in figure 2 for MNOS structures with 300 μm square dimensions. The anneal time is 60 min. A decrease of N_{ss} with increasing temperatures is observed [6]. A minimum N_{ss} -value is found at 1 000 °C. For temperatures higher than 1 050 °C etching of the nitride layer takes place during the hydrogen anneal.

FIG. 2. — Anneal temperature dependence of fast surface state density N_{ss} for hydrogen anneals of 300 μm square MNOS structures. Anneal time is 60 min.

3.2 ANNEAL TIME EFFECTS. — The results of hydrogen anneals at 950 °C for different anneal times on the same 300 μm square MNOS structures are shown in figure 3. A decrease of N_{ss} with increasing anneal

FIG. 3. — Anneal time dependence of fast surface state density N_{ss} for hydrogen anneals of 300 μm square MNOS structures. Anneal temperature is 950 °C.

time is observed [6]. From the data in figures 2 and 3 it is obvious that a longer anneal at a lower temperature can be as effective as or even more effective than an anneal at a higher temperature. This can be useful in some cases, for instance, where we want to preserve some critical impurity diffusion profiles.

3.3 GEOMETRY EFFECTS. — Figure 4 shows the effect of a hydrogen anneal at 900 °C for 60 min. on square MNOS structures with different dimensions. A marked geometry effect is observed. The smaller the structure dimensions, the lower will be the corresponding N_{ss} -value and this for any anneal condition (temperature and time). In other words, the described high-temperature hydrogen anneal is indeed characterized by a lateral diffusion process. In the case of smaller structures, the hydrogen, passing through the cutouts in the nitride layer, has to diffuse over shorter distances under the nitride gate in order to reach the center of the active MNOS region, than in the case of the larger structures. The technique is therefore more suitable in reducing the density of fast surface states under gates with relatively small dimensions.

FIG. 4. — Dependence of fast surface state density N_{ss} on the dimension of square MNOS structures for hydrogen anneals at 900 °C for 60 min.

The smallest dimension of the structure determines the effectiveness of the hydrogen anneal. This is obvious when we compare figure 4 with figure 5, which shows the effect of a hydrogen anneal under the same conditions as in figure 4 (900 °C, 60 min) on MNOS structures with a smallest dimension of 100 μm and with the other dimension varying between 100 μm and 1 000 μm.

3.4 LATERAL DIFFUSION EFFECTS. — As a result of the lateral hydrogen diffusion, the anneal is found to

FIG. 5. — Dependence of fast surface state density N_{ss} on the largest dimension of MNOS structures with a smallest dimension of 100 μm. Hydrogen anneal conditions are 900 °C and 60 min.

be incomplete for structures with relatively large dimensions, resulting in a non-uniform N_{ss} profile under the nitride gate. Only the edge region of the structure is completely annealed, showing a N_{ss} -value lower than $10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ (Fig. 6). With a specially designed device the width w of this edge region is determined to be 85 μm after an anneal at 950 °C for 60 min. This means that MNOS structures with a smallest dimension of 170 μm are completely annealed at 950 °C, resulting in a N_{ss} -value lower than $10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ over the total structure area.

For smaller dimensions, for instance in the case of MNOS transistors, where the H_2 -anneal can be performed through the contact holes, lower anneal temperatures (≤ 800 °C) and/or shorter anneal times (15 min.) will suffice to reduce N_{ss} below $10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ under the transistor gate. Indeed, the distance between a contact hole and the center of the channel region is typically 15 μm, which is very much smaller than the 85 μm, previously mentioned. This result is important since a lower temperature range is

FIG. 6. — Non-uniform N_{ss} -profile as a result of the lateral hydrogen diffusion mechanism.

also needed in order to preserve good quality of the silicon nitride layer in view of its memory retention capability [7].

3.5 VERTICAL DIFFUSION EFFECTS. — For the MNOS structure of figure 7, N_{ss} -measurements on the inner 100 μm square aluminum gate G, after H_2 -anneals of 60 min. at different temperatures in the 900-1 050 $^{\circ}\text{C}$ range, give the path of figure 8. Although this inner gate lays far enough from the nitride gate edge, so that lateral diffusion effects can be ignored, a reduction of the density of fast surface states is observed under this inner gate. This means that hydrogen has the possibility to diffuse through the nitride layer. This vertical diffusion mechanism depends strongly on the silicon nitride density. The result is a uniform reduction of N_{ss} over the total MNOS device area, but it is hard to go below $10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ for N_{ss} , as is the case with the lateral diffusion mechanism.

FIG. 7. — Large MNOS structure with ring-shaped aluminum gates for illustration of the vertical hydrogen diffusion mechanism through the nitride layer.

FIG. 8. — Anneal temperature dependence of fast surface state density N_{ss} under the G-gates of the MNOS structures of figure 7. Anneal time is 60 min.

4. Summary. — In order to reduce the density of fast surface states in MNOS structures by means of a high-temperature hydrogen anneal, the silicon nitride next to the active MNOS regions is removed, so that the hydrogen can penetrate into the active regions from where it migrates to the SiO_2 -Si interface, where it annihilates the fast surface states.

Summarizing, the results indicate that :

- 1) A maximum reduction of N_{ss} after a 1 hour anneal occurs at 1 000 $^{\circ}\text{C}$, but a longer anneal at a lower temperature can be as effective as or even more effective than an anneal at a higher temperature.
- 2) A marked geometry effect is observed as a result of this lateral hydrogen diffusion mechanism.
- 3) Structures with a smallest dimension of 170 μm can be completely annealed at 950 $^{\circ}\text{C}$.
- 4) Besides this lateral diffusion process, a vertical diffusion through the nitride layer is observed at temperatures above 850 $^{\circ}\text{C}$.

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