SUPPRESSION OF OUT-DIFFUSION EFFECT OF DOPANTS BY THE HfO_2 DIFFUSION BARRIER FOR HIGHLY *N*-DOPED GE EPILAYERS GROWN ON SI(001) SUBSTRATE

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ABSTRACT

Ge is a potential candidate for the realization of Si-based light sources that are compatible with CMOS technology. Electron doping in Ge is an efficient method to modify its band gap structure to enhance the radiative recombination of Ge film. Post growth thermal treatment is a necessary step to activate the dopants and ameliorate the film’s crystal quality. Thermal annealing process at high temperature resulting the out-diffusion effect of dopant, such as Sb or P element. In this paper, we present the role of diffusion barrier using HfO_2 layer on the prevention of the dopant segregation on the surface. The Ge film is grown on Si substrate by molecular beam epitaxy (MBE) technique. It is worth noting that in the case of n-doped Ge epilayers with the HfO_2 barrier, the PL intensity increases by a factor of 1.6 compared to that of the free barrier sample. However, tensile strain in Ge film is not affected by the HfO_2 layer and remains the value of about 0.20% after annealing at 750°C in 60 secs.

Key words: *n-doping; out-diffusion; HfO_2 barrier; Photoluminescence; tensile strain*

INTRODUCTION

As an indirect band gap material, the electronic structure of germanium exhibits very interesting feature, that is the direct valley (Γ) is only at 0.14 eV above the indirect one (L)[1]. One of an effective method to compensate the energy difference between Γ and L valleys is to fill the indirect conduction valley by n-type doping, which leads to a more efficient population of the zone center and thus enhances radiative recombination at the Γ valley [2]. The free carriers induced by the dopants will occupy the lowest energy levels of the conduction band (L valley). Under an external excitation, the generated carriers can now occupy higher energy levels. Consequently, the energy difference between L and Γ valleys is now seen, by the pumped electrons, smaller comparing to the case of intrinsic germanium. It has been shown that by the combination of moderate tensile strain of 0.25% and an extrinsic electron density of $7.6x10^{19}$ cm^{-3}, by n-type doping, the Fermi level reaches the bottom of the direct band gap [3]. The energy gap of Ge thus can be considered of a direct nature.

For n-doping process in Ge film, one can use V group elements such as As, P or Sb. Post thermal annealing after MBE doping process is an essential step in order to activate the dopant atoms into the substitutional sites of the Ge matrix. This step is particularly important in the case of a low-temperature doping along which a great part of dopant atoms is incorporated in the interstitial sites of the Ge lattice. When the Ge is only doped with phosphorus, we have deduced from SIMS measurements a total phosphorus concentration of $2x10^{20}$ cm^{-3} [4]. Based on the shift of the PL spectra, an activated phosphorus concentration of $2x10^{19}$ cm^{-3} [4]. The most optimal annealing condition for phosphorus is about 750°C during 60 sec. Above 750°C, we observe an important evaporation of phosphorus from the Ge film surface.

When a second doping element (Sb) is added, the annealing condition become more complicated. This is because antimony has a higher diffusivity than that of phosphorus. Experimentally, we have observed that Sb starts to desorb from the Ge surface at around 680°C. Thus, if a sample, which is co-doped

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with P and Sb, is annealed at 650°C, a part of P atoms has been not activated. It is therefore important to find out a way to efficiently activate both dopant atoms, in particular to prevent the out-diffusion of antimony when annealing is carried out at a temperature higher than 700°C. The diffusion barriers were commonly used in the semiconductor technology to limit the out-diffusion of doping elements [5]. Depending on the nature of the materials, the diffusion barrier should not be chemically reactive. Also, it must provide a strong adhesion on the film surface. Hafnium oxide is known to be one of the most important high-k materials used in semiconductors industry, which has enabled further scaling of the CMOS integrated circuits by replacing silicon dioxide as a gate dielectric [6].

In this work, we use a HfO_2 thin layer as a diffusion barrier to reduce the out-diffusion effect of Sb and P dopants occuring in the thermal annealing process after epitaxial growth.

EXPERIMENT DETAILS

Ge growth was performed in a standard solid source MBE system with a base pressure better than $5x10^{-10}$milibars. The growth chamber is equipped with a 30 keV reflection high-energy electron diffraction (RHEED) apparatus allowing monitoring in real time the Ge growth mode. An Auger electron spectrometer (AES) is used to control the cleanliness of the substrate surface prior to growth and the film composition. Ge was evaporated from a two-zone heated Knudsen effusion cell to avoid Ge condensation at the upper part of the cell crucible, thus insuring a highly stable Ge deposition rate. The Ge deposition rate, measured using RHEED intensity oscillations during Ge homoepitaxy on a Ge (111) substrate, was in the range from 1.5 to 5 nm/min The substrates were flat, p - type Si (001) wafers. Cleaning of the substrate surface followed the hydrogen terminated Si (001) method, which consists of two steps: the first is a wet chemical treatment in NH_4 F solution to prepare an ideally SiH_2 - terminated Si (001) surface [7]. The second step is an annealing in ultrahigh vacuum to desorb the passivating hydrogen layer at a temperature of about 500^{o}C. After this step, the Si surface exhibits a well-developed 2x1 reconstruction and AES measurements do not reveal any presence of oxygen or carbon. The substrate temperature was measured using a thermocouple in contact with the backside of Si wafers. These measurements were corrected using an infrared pyrometer (Ircon, W-series) operating in the wavelength region of 0.90–1.08 μm, in which the emissivity of Si is constant. The accuracy of the temperature measurement is estimated to be about ・20^{o}C.

Structural analysis of post-grown films was performed by means of high-resolution transmission electron microscopy (HRTEM) using a JEOL 3010 microscope operating at 300 kV with a spatial resolution of 1.7Å.

The strain level in the Ge epilayers was deduced from X-ray diffraction (XRD) measurements performed using a diffractometer (Philips X'pert MPD) equipped with a copper target for $Cu\text{-}K_{\alpha1}$ radiation (□λ=1.54059°). The angular resolution is ~0.01.

The PL is measured with a 532 nm laser focused on the sample surface. The PL signal is measured with an InGaAs detector and the wavelength is cut off at 1600nm.

After Ge film growth, samples were transferred to another deposition system available in CINaM and a 150 nm thick Hafnium oxide (HfO_2) was deposited using Atomic Layer Deposition (ALD) technique.

RESULT AND DISCUSSION

For n-doping process, we employ the co-doping technique using P and Sb elements in which P atoms are produced by the decomposition of the GaP solid source. As high diffusion coefficient elements, in the P and Sb co-doping process, the growth temperature is a key parameter determining the dopant concentration as well the PL intensity of the Ge film. Figure 1 displays RHEED patterns taken after 450 nm thick co-doped Ge films at substrate temperatures of 140, 170 and 200°C, respectively. Starting from a 2D (2x1) RHEED pattern of the intrinsic Ge buffer layer, we observe the RHEED pattern remains unchanged during co-doping at 200°C. When the substrate temperature reduces to 170°C (Fig. 1b), while the RHEED pattern still shows a streaky feature, some intensity reinforcements have appeared at the position corresponding to bulk-like 3D spots. In particular, with further decrease of the substrate temperature down to 140°C (Fig. 1c), the diffraction streaks are found to gradually vanish and diffraction rings appear, indicating the polycrystalline nature of the doped Ge film.

During the doping process in Ge, we have established a correlation between RHEED patterns and PL properties: when the film growing surface is 3D, the PL response of the corresponding layer degrades. Combining with the results from the PL evolution on the substrate temperature (not shown here), we set up the growth temperature for the n doped Ge film at 170^{o}C.

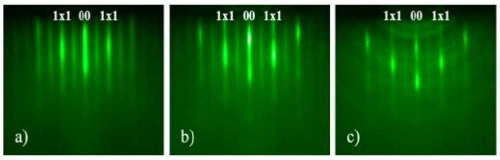

Figure 1. *RHEED patterns taken along [110] azimuth after 100 nm thick, P and Sb co-doped Ge film grown on Si (001) at temperatures of 200°C (a), 170°C (b) and 140°C (c)*

Figure 2a shows a TEM image of the as-grown Ge film doped with P and Sb and then capped with hafnium oxide at a substrate temperature of about 100°C. The as-deposited Ge film has a thickness of about 450 nm and contains a high density of threading dislocations. However, its surface is smooth and thus the interface between Ge and HfO_2 is relatively abrupt. After growth, the samples were annealed in a RTA (Rapid Thermal Annealing) furnace in an Argon gas at 750°C for 1 min. The temperature was increased with a ramp of 25 °C/s (Figure 2b).

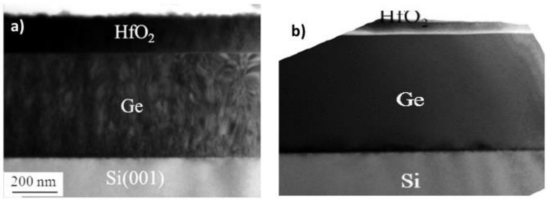

Figure 2. *a) Cross sectional TEM image of the Ge film co-doped with Sb and P at 170 °C, and capped with 150 nm thick of HfO_2.*

b) Cross-sectional TEM images of 450 nm thick Ge films co-doped with Sb and P and capped with 150 nm thick of HfO_2, and then annealed at 750°C during 1 min

It can be seen from the image that upon annealing a significant decrease of the threading dislocations density is observed. The sample displays a relatively smooth interface.

We now discuss the role of the diffusion barrier layer on the dopant out-diffusion in the case of Ge/Si growth. To better see this effect, we show in Figure 3 a comparison of two identical Ge samples, which have been co-doped with P and Sb on Si substrate at the same temperature (170°C).

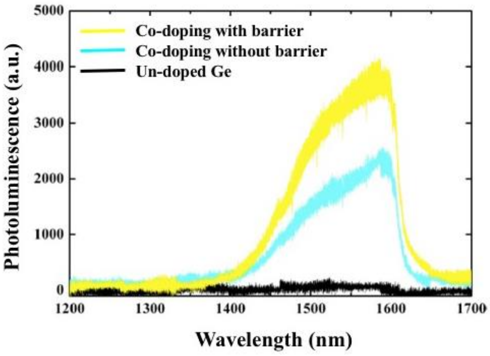

Figure 3. *Comparison of photoluminescence spectra of two identical samples of 1 µm thick co-doped Ge films grown at 170 °C, one is capped with HfO_2 (yellow curve) and the other is without capping layer (cyan curve)*

The first sample is capped with 100 nm thick HfO_2 layer and the second one is let without

HfO_2 capping. Rapid thermal annealing at 650°C (1min) was done for the two samples. It can be clearly seen that the sample capped with HfO_2 exhibits an enhancement of the PL intensity by a factor of 1.6 compared to that of the sample without capping layer. This result demonstrates the significant role played by the capping layer in minimizing the loss of dopants associated with the indispensable annealing step, by which we annihilate the most of dislocations present in the as-grown Ge films on silicon. We note that the wavelength corresponding to the indirect band gap of Ge should be located above 1650 nm, which is out of the spectral range due to the detector cut off.

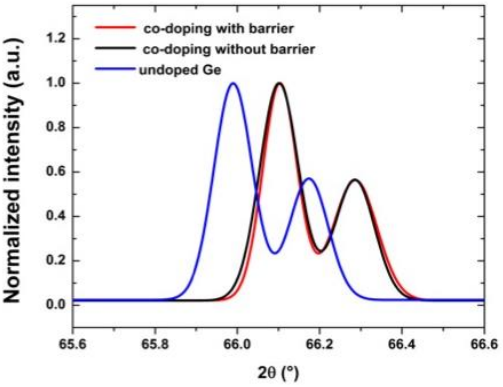

Figure 4. C*omparison of θ-2θ XRD scans around the Ge (004) reflection measured for co-doped Ge samples capped with* HfO_2*, after annealing at 850°C for 1 min. The blue curve scan represents a Ge bulk substrate*

It has been shown that when apply a tensile strain in Ge film, the energy difference between the zone centre valley and the direct L valley will be reduced [3, 8]. In this work, tensile strain induced by taking benefit of the thermal mismatch between Ge and Si[2-3, 9-14]. We investigate the effect of rapid thermal annealing on the tensile strain level of capped Ge films grown on Si substrate. Figure 4 displays θ-2θ XRD scans around the Ge(004) reflection of Ge samples capped with three diffusion barriers, after annealing at 750°C for 1 min. For comparison, we also show the (004) reflection of a Ge bulk substrate (blue curve).

Interestingly, the tensile strain, deduced from the XRD measurements, is about 0.2% for Ge film with and without the HfO_2 diffusion barrier. This result implies that the tensile strain level inside the Ge film mainly depends on the annealing conditions and is not affected by the upper capping layer.

CONCLUSION

In summary, we have grown highly n-doped Ge epilayers on Silicon substrate with the HfO_2 diffusion barrier by MBE and ALD techniques. The growth temperature is in the range of 140-200^{o}C and at the temperature of about 170^{o}C, the PL intensity obtained the highest value. Concerning to the efficiency of the HfO_2 barrier in the suppression of dopant's out-diffusion, it is shown that the sample capped with HfO_2 exposes an enhancement of the PL intensity by a factor of 1.6 compared to that of the sample without capping layer. This result demonstrates the significant role played by the capping layer in minimizing the loss of dopants associated with the indispensable annealing step. Regarding the tensile strain value, the X-ray diffraction measurement shows that the tensile strain level inside the Ge film mainly depends on the annealing conditions and is not affected by the upper capping layer.

ACKNOWLEDGMENTS

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.02-2015.106. We also thank Prof. V. Le Thanh at the Aix-Marseille University and his group for supporting this work.

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ABSTRACT

KHỐNG CHẾ HIỆU ỨNG KHUẾCH TÁN NGOÀI CỦA NGUYÊN TỐ PHA TẠP BẰNG HÀNG RÀO KHUẾCH TÁN HFO$_2$ CHO MÀNG GE PHA TẠP ĐIỆN TỬ NỒNG ĐỘ CAO TĂNG TRƯỞNG TRÊN ĐẾ SI(100)

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Ge là một ứng viên tiềm năng trong việc hiện thực hoá những nguồn phát sáng trên cơ sở silic tương thích với công nghệ CMOS. Pha tạp điện tử trong lớp Ge là một phương pháp hiệu quả để thay đổi cấu trúc vùng cấm của nó nhằm cải thiện khả năng phát huỳnh quang của màng Ge. Xử lý nhiệt sau khi tăng trưởng là một bước cần thiết để kích hoạt các nguyên tố pha tạp cũng như cải thiện chất lượng tinh thể. Quá trình xử lý nhiệt ở nhiệt độ cao dẫn tới hiệu ứng khuếch tán ngoài của các nguyên tử pha tạp, ví dụ như nguyên tố Sb hoặc nguyên tố P. Trong bài báo này, chúng tôi trình bày về vai trò của hàng rào khuếch tán sử dụng lớp HfO_2 để ngăn cản sự di chuyển của nguyên tử pha tạp lên trên bề mặt mẫu. Màng Ge được chế tạo bằng kỹ thuật epitaxy chùm phân tử. Đáng chú ý là trong trường hợp màng Ge pha tạp điện tử có hàng rào khuếch tán thì cường độ huỳnh quang tăng gấp 1,6 lần so với mẫu không có hàng rào khuếch tán. Tuy nhiên ứng suất căng trong màng Ge lại không bị ảnh hưởng bởi lớp HfO_2 và vẫn duy trì giá trị là 0,20% sau khi được xử lý nhiệt ở 750^{o}C trong thời gian 60 giây.

Từ khoá: *Pha tạp điện tử; khuếch tán ngoài; hàng rào HfO2; huỳnh quang; ứng suất căng*

Ngày nhận bài: 26/3/2018; Ngày phản biện: 06/4/2018; Ngày duyệt đăng: 31/5/2018

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