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Diffusion and electrical activity of copper in $Si_{1-x-y}Ge_xC_y$ alloys

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Abstract

We investigate copper diffusion in Si-rich $Si_{1-x-y}Ge_xC_y$ ($x<20\%$) and Ge-rich ($x=93\%$) $Si_{1-x}Ge_x$ layers. The profiles of the different constituents (Si, Ge, Cu, C, B) were determined using secondary ion mass spectroscopy (SIMS). Carrier profiles were studied by electrical characterizations of Schottky diodes. The structures were prepared by copper deposition on SiGeC alloys at room temperature. The increase of the Ge-content from 0% to 93% results in a decrease of the Cu diffusion depth determined by SIMS. C-incorporation also leads to a reduction of Cu-diffusion. The effect of boron seems to be more important, and Cu-diffusion is well retarded in p-type samples. The electrical activity of Cu in IV–IV alloys depends on the Ge-content. For Si-rich p-type SiGe alloy, we observed a passivation of the boron acceptors attributed to the formation of Cu–B pairs, which also explains the reduction of Cu diffusion. For p-type Ge-rich samples, the acceptor concentration can reach very high values (larger than the boron concentration), and becomes temperature dependent. These results show that boron passivation is no longer the most important effect of Cu diffusion. We suggest that the presence of Cu in Ge-rich alloys produces an acceptor-like trap.

Keywords: Cu; SiGeC; Boron passivation; Trap

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1. Introduction

Numerous investigations have shown that copper is a promising candidate to replace Al in future interconnect technology. Unfortunately, Cu exhibits exceptional fast diffusion in silicon and

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germanium. It also can create deep level traps and even a rather shallow level in Ge at $E_v + 0.04$ eV [1]. Even at room temperature, copper diffuses as a positively charged interstitial in Si, and can form pairs with boron and thereby leads to the passivation of the boron electrical activity [2]. It has also been shown [3] that this complex formation reduced the diffusion coefficient of interstitial copper in p-type silicon.

In a recent work [4], we investigated copper passivation of boron in $Si_{1-x}Ge_x$ layers with $x \leq 30\%$, using electrical characterization of Schottky diodes. The mechanisms for passivation seem similar to those evidenced for pure silicon: the fast-diffusing interstitial Cu^+ passivates the boron acceptors by forming neutral B–Cu pairs. We have shown that the Cu diffusivity is retarded by increasing the Ge-content. In addition, Cu diffusion is very sensitive to the presence of dislocations located at the interface between the (partially/totally) relaxed SiGe layers and the Si substrate.

In this work, we use SIMS measurements to monitor the Cu diffusion and to correlate quantitatively the Cu-content with the boron activity. We have extended our investigations to Ge-rich SiGe alloys and have studied also the influence of Ge (low and high content) on Cu diffusion and its electrical activity in group-IV compounds.

Recently, it was shown [5] that carbon doping can be used to suppress diffusion of B and P and enhance diffusion of As and Sb in Si. This effect is due to undersaturation of Si self-interstitials and supersaturation of vacancies caused by outdiffusion of C. Therefore, carbon can be used to suppress diffusion of dopants in Si-based devices when this diffusion occurs via an interstitial mechanism. Recently, the impact of C incorporation on the diffusion of B in SiGe:C heterojunction bipolar transistors has been studied [6]. The diffusion of B was found to be strongly reduced due to the presence of C on substitutional sites [7] and it has been shown that the diffusion is suppressed when the concentration of C is enhanced to about 10^{19}–10^{20} cm^{-3} [8]. Therefore, we include some analyses to see if such a beneficial impact of C incorporation can also be observed for Cu diffusion.

2. Experimental details

Epitaxial $Si_{1-x-y}Ge_xC_y$ layers, with x ranging from 0 to 93% and y from 0 to 1.7%, were grown either by rapid thermal chemical vapor deposition (RTCVD) or molecular beam epitaxy (MBE) on Si(100) substrates. The composition and the thickness of each layer have been determined by Rutherford backscattering spectrometry (RBS) with a fitting procedure. Two different structures were grown for this study. The first set of samples consists of thin pseudomorphic layers with Ge-content ranging from 0 to 13%. The thickness of these films was typically 100 nm. The second set of samples includes thicker layers ($t > 200$ nm) for capacitance–voltage (C–V) measurements. These samples are either partially or totally relaxed depending on the Ge-content. The threading dislocation density is expected to increase with film thickness. Prior to metal deposition, each sample was cleaned using a standard degreasing procedure, followed by a dip in diluted HF for 30 s and a final rinse in deionized water. After a rapid loading, 100 nm-Cu films were deposited at room temperature in a magnetron sputtering system, and through a shadow mask for electrical characterizations. The Cu films were not annealed after deposition. C–V measurements were performed at 1 MHz with samples held at temperatures in the range 100–200 K. The carrier concentration depth profiles were obtained by using the relation $dC^{-2}/dV = 2/[qA^2\varepsilon_s N_A(w)]$ [1], where q is the elementary charge, A is the diode area, ε_s is the permittivity of the SiGe alloy, and $N_A(w)$ is the carrier concentration at a depth w. Some characterizations were performed on tungsten–Schottky diodes for comparison. The measurements have been performed at low temperature to limit the current in the low-barrier Schottky diodes. SIMS investigations were performed using a CAMECA IMS-4F ion microscope with an O_2^+ primary ion beam. The boron and copper concentrations were determined in reference to implanted silicon standards. This procedure is valid for Si-rich films [9]. Meanwhile, for Ge-rich layers matrix effects on the ionization yield should be taken into account for correct quantifications. For SIMS analyses of the films, the copper films have been removed to limit the ion mixing in the epilayers.

3. Results and discussion

In Fig. 1, we show the Cu depth profiles determined by SIMS in p-type films with Ge-content ranging from 0 to 93%. The Si-rich layer exhibits the same boron-doping level (2.5×10^{16} cm^{-3}) as the silicon film, while this doping-level is lower in the Ge-rich film (1.5×10^{15} cm^{-3}). The increase of the Ge-content from 0 to 13% results in a decrease of the Cu diffusion depth determined by SIMS. The stress retained in the film due to the Ge can also contribute to the reduction of the Cu diffusion. Although the boron content is lower, the reduction is even more pronounced in the relaxed-$Si_{0.07}Ge_{0.93}$ film, suggesting a chemical effect due to Ge-incorporation. Such a chemical effect on diffusion, has also been reported by Rajendran et al. [10], who have shown that the diffusivity of boron in $Si_{0.85}Ge_{0.15}$ is an order of magnitude lower than that in Si.

In order to separate Ge, C and B effects, similar SIMS measurements have been carried out on n-type $Si_{0\ 87}Ge_{0.13}$ with and without 1.7% of C. The Cu profile in the binary alloy is similar to that obtained in the p-type pure-Si, while that in the C-containing alloy is similar to the p-type $Si_{0.87}Ge_{0.13}$ indicating that about 10^{-4}% of B are as effective as 13% of Ge or 1.7% of C to limit Cu diffusion in silicon. Rücker et al. [5] reported that the effect of C on dopant diffusion is due to non-equilibrium densities of silicon self-interstitials and vacancies caused by coupled diffusion of C and Si point defects. A significant carbon diffusion in silicon requires elevated temperatures (much higher than in

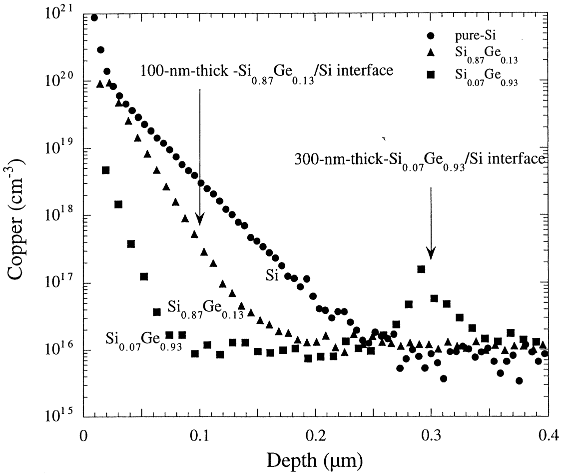

Fig. 1. SIMS Cu profiles in p-type Si, 100 nm-$Si_{0.87}Ge_{0.13}$ and 300 nm-$Si_{0.07}Ge_{0.93}$ films.

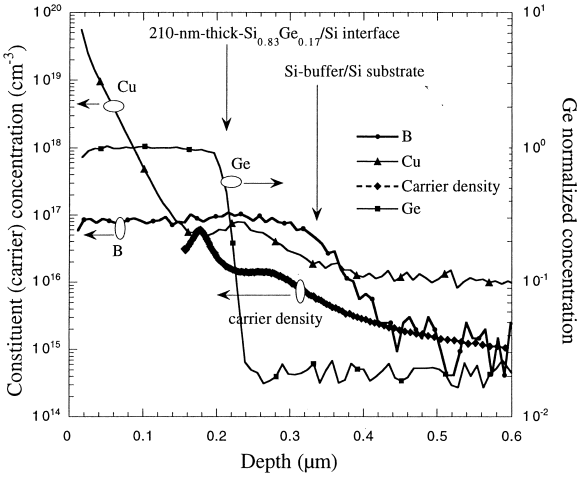

Fig. 2. Active acceptor concentration depth profiles obtained by *C–V* measurements at 120 K for the as-deposited Cu/p-type 210 nm-$Si_{0.83}Ge_{0.17}$ and SIMS profiles for Cu, B and Ge.

our experiments). Surprisingly, we found that even nondiffusing carbon impacts the copper diffusion at room temperature. On the other hand, the negatively charged boron acceptors are very efficient to limit Cu-diffusion.

Electrically active acceptor profiles have been determined by *C–V* measurements on Cu/partially relaxed p-type $Si_{0.83}Ge_{0.17}$ Schottky diodes (Figs. 2, 3). The SIMS profiles for Cu, B and Ge are also given for comparison. The strain relaxation in the sample has occurred by generation of misfit

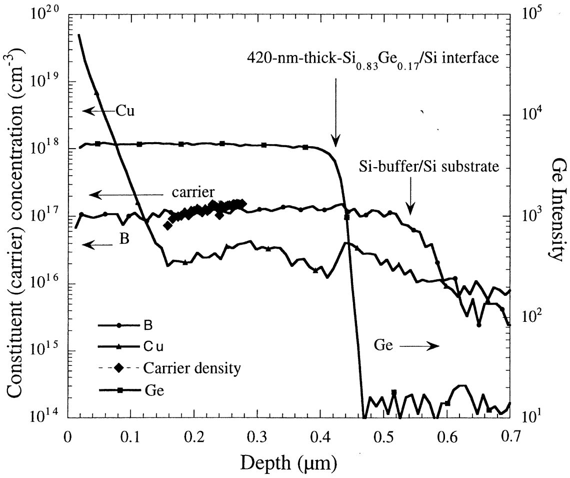

Fig. 3. Active acceptor concentration depth profiles obtained by *C–V* measurements at 120 K for the as-deposited Cu/p-type 420 nm-$Si_{0.83}Ge_{0.17}$ and SIMS profiles for Cu, B and Ge.

dislocations at the film/Si substrate interface. Figs. 2 and 3 clearly show that Cu accumulates at this interface, that is along the dislocations. This phenomenon is well-known and has been evidenced in samples after Cu-diffusion at high temperature followed by rapid quenching [11]. A significant reduction of the boron activity is observed towards the surface and the Si interface for the 210 nm-thick film. This reduction occurs only when the Cu content is larger or similar to the boron level. This trend is confirmed by results obtained for the 420 nm-thick $Si_{0.83}Ge_{0.17}$ layer. For this sample, the carrier profile is obtained in an area where the Cu content is lower than that of B and therefore too small to deactivate the boron. For the Si-rich SiGe alloy, we observed a passivation of the boron acceptors. Moreover, this effect does not exhibit any temperature dependence. These results are very similar to those reported for Cu on boron-doped Si, and suggest that the highly mobile interstitial Cu^+ passivates the boron acceptor by forming a neutral Cu–B complex rather than by direct compensation.

The behavior of Cu-contacts to p-type $Si_{0.07}Ge_{0.93}$ is quite different (Fig. 4). For comparison, we performed similar analyses on W-contacts on this Ge-rich alloy. For such contacts, the doping profiling yields the expected boron concentration which does not depend on temperature. The acceptor concentration in the Cu-sample is no longer lower than the boron concentration ($\approx 10^{15}$ cm^{-3}, obtained from SIMS and *C–V* measurements on the W-sample). The active acceptor concentration can reach very high values depending on temperature. These results cannot be explained in terms of boron deactivation (as for the Si-rich samples). We suggest that the presence of Cu in Ge-rich samples produces an acceptor-like trap. The trap level crosses the Fermi level at a distance *d* below the surface. For distance less than *d* the traps are ionized and the space charge density is larger than the boron concentration. The observed temperature dependence must be due to the emission rate variation with temperature [12]. The trap may or may not follow the small amplitude 1-MHz-signal when the temperature is changing. It is important to note that the depth, calculated from the capacitance is not the actual depletion depth in this case. The acceptor concentration (Fig. 4) which seems to exist in the Si-substrate accounts, in fact, for phenomena which occur towards the surface and at the interface where the Cu-concentration is high (Fig. 1).

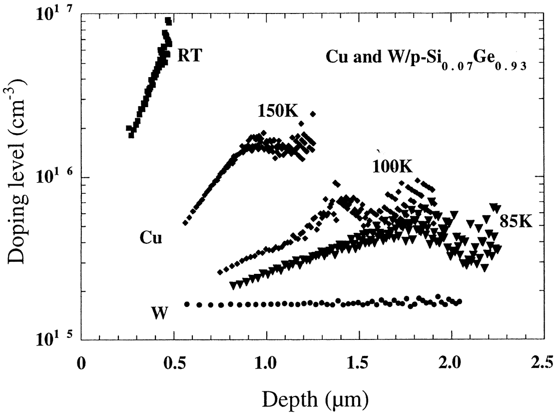

Fig. 4. Acceptor concentration depth profiles obtained by *C–V* measurements at different temperatures for as-deposited Cu/p-$Si_{0.07}Ge_{0.93}$ sample.

4. Conclusion

We have investigated Cu diffusion in SiGe layers by using electrical characterizations of Schottky diodes and SIMS measurements. We found a chemical effect on Cu diffusion due to the presence of Ge. C-incorporation also leads to a reduction of Cu diffusion. Passivation of the boron acceptors occurs after copper deposition at room temperature in Si-rich layers. The mechanisms for boron passivation seem to be similar to those found for pure silicon: the fast-diffusing interstitial Cu^+ passivates the boron acceptor by forming a neutral B–Cu complex. For Ge-rich films, we suggest that Cu produces an acceptor-like trap with a temperature dependent emission rate.

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