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Surface activation using oxygen and nitrogen radical for Ge–Si Avalanche photodiode integration

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ABSTRACT

In this work, an alternative method for producing the single crystalline Ge–Si Avalanche photodiodes (APD) with low thermal budget was investigated. Structural and electrical investigations show that low temperature Ge to Si wafer bonding can be used to achieve successful APD integration. Based on the surface chemistry of the Ge layer, the buried interfaces were investigated using high resolution transmission electron microscopy as a function of surface activation after low temperature annealing at 200 and 300 °C. The hetero-interface was characterized by measuring forward and reverse currents.

1. Introduction

Avalanche photodiodes (APD) are used to detect and amplify weak optical signals using the internal gain provided by the impact ionization process [1]. They have been used widely in optical communication systems. These components have been available for several years from the III/V semiconductor technology on Indium Phosphide (InP) and Gallium Arsenide (GaAs) wafers [2]. Nevertheless, the integration of these devices on large wafers within the mainstream silicon technology requires either high-cost hybrid integration approach or back-end technology. Pure single crystalline germanium is a promising candidate for a broadband photodetector [3,4]. The integration of germanium (Ge) into silicon (Si) increases absorption, leading to possible photodetection at telecommunication wavelengths (from 1.31 to 1.55 μm). Furthermore, germanium has a direct energy bandgap of 0.8 eV and is compatible with the CMOS technology. However, conventional epitaxial Ge growth requires careful processing and device design to minimize the impact of the dislocations. Such defects and dislocations are generation centers that contribute to low efficiencies [5].

Ge to Si direct bonding has been studied for use in high-performance APD as well as high-quality epitaxial templates for GaAs growth [6,7]. In order to establish this Ge–Si APD technology, one of the most crucial issues is to reduce dark current by means of the formation of interfaces with a low defect density [8]. Therefore the characterization of bonded Ge–Si hetero-interfaces is a matter of the utmost importance for APD applications. Up to now physical properties of directly bonded Ge–Si interfaces received little attention. The native oxide of Ge substrates is thermodynamically difficult to control due to its poor thermal stability and water solubility. This paper intends to clarify the Ge–Si interface properties, their dependencies on the surface activation conditions, and their impact on the current–voltage (*I*–*V*) characteristics of Ge–Si hetero-structure.

The Ge surface chemistry after radical activation and the bonding energy have been previously reported by our group [9]. Based on the surface chemistry of Ge surface, we investigate the properties of the buried interface as a function of radical surface activation and characterize the Ge–Si heterojunction by measuring the forward and reverse currents.

2. Experimental

In this experiment, 4-inch (1 0 0)-oriented p-type Ge wafer (Ga doped, resistivity = 0.016 Ω cm) and (1 0 0)-oriented n-type Czochralski grown bare Si wafers (P doped, resistivity = 2–4 Ω cm) were selected for direct wafer bonding. Prior to bonding, the Ge and Si wafers were cleaned in an Standard Clean 1 (SC1)-equivalent solution with and without ozone for Si and Ge, respectively. Wafers were loaded into an Applied Microengineering Limited (AML) AW04 aligner bonder and vacuum was applied. The wafers were exposed for 10 min to either oxygen or nitrogen free radicals (the chamber pressure was 1 mbar at 100 W) generated by a remote plasma ring [10]. After activation, the Si and Ge wafers were bonded in situ under a pressure of 1 kN applied for 5 min at a chamber pressure of 10^{-5} mbar. The wafers were annealed in situ at 100 °C for 1 h with an applied pressure of 500 N. This operation was followed by an ex situ anneal at 200 °C for 24 h in order to

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enhance the bond strength. The bonded pairs were then annealed again at 300 °C for 24 h. The ramp-up rate was set to 0.5 °C/min in both cases. After anneals, Ge–Si bonded pairs remained intact in spite of their coefficient of thermal expansion (CTE) mismatch. The bonded interfaces were imaged by high resolution transmission electron microscopy (HR-TEM), while the electrical properties of p-Ge/n-Si bonded hetero-structure was investigated by measuring *I–V* characteristics with gold (Au) and indium (In) metal contacts on the Ge and Si sides, respectively.

In the second part of the experiment, p-type Ge wafers were bonded directly to B-doped p/p + epi-Si wafers (resistivities of 10 μm-epi layer and substrate are 10–16 Ω cm and 0.02 Ω cm, respectively) using the same pre- and post bonding conditions, i.e. 10 min oxygen radical activation at low temperature. Prior to surface activation, all wafers were cleaned in a SC1-equivalent solution, rinsed in de-ionized (DI) water and dried in a spin-dryer. After anneal at 200 and 300 °C the Ge–Si heterojunction of bonded pairs was characterized by measuring the forward and reverse current with Au metal contacts on Ge wafers and In metal contacts on epi-Si wafers.

3. Results and discussion

3.1. Chemical and structural characterization

Fig. 1 shows the Angle-Resolved X-ray Photoelectron Spectroscopy (ARXPS) analysis of the Ge 2p3/2 shape profile of activated Ge surface by radical (take-off angle = 0°, 75°). As expected the Ge 2p3/2 signal shows two binding energy contributions at 1218.5 and 1221.0 (±0.2) eV [11]. These can be assigned to zero- and approximately quadra-valent Ge respectively and suggest the presence of a GeO_2 layer at the substrate surface. This is confirmed as moving towards grazing emission (take-off angle = 75°) the relative contribution of the quadra-valent Ge is increased, which corresponds to GeO_2 (Fig. 1 right). The contribution from the oxide is somewhat more in the Ge 2p3/2 data because of the greater surface sensitivity of the Ge 2p3/2 data where the kinetic energy of the photoelectrons is around 260 eV which, the minimum of the universal inelastic mean free path curve, i.e. Fig. 1 suggests that even very short radical exposure of hydrophilic cleaned germanium substrates enhances the surface oxidation [9].

In addition, the interface of the Ge/Si hetero-structures was analyzed by HR-TEM. The interface is seen as a white band with thickness about 2 nm. From Fig. 2, the buried oxide thicknesses of reference sample, oxygen and nitrogen radical activated samples were measured to be 13, 16 and 22 Å, respectively. This suggests that radical activated Ge can generate thicker GeO_2 by means of radical activation and promotes further hydrophilic reaction during anneal. TEM micrographs also indicate that buried oxides are quite smooth and their thickness is uniform. It has been reported that dislocations can be generated in directly bonded Ge/Si without an amorphous oxide due to the relaxation of the large lattice mismatch [6]. On the contrary, from these TEM micrographs (Fig. 2), dislocations are not observed at the interface or bulk regions. The strain caused by the large lattice mismatch and difference in the coefficient of thermal expansion (CTE) between Ge and Si is considered to be very low due to the amorphous interfacial layer and low thermal budget enabled by remote plasma activation.

3.2. Electrical characterization

The *I–V* characteristics of directly bonded interfaces were measured using Au and In metal contacts. Fig. 3 shows the forward *I–V* curves of p-Ge/n-Si heterojunctions for the reference and radical activated bonded pairs after anneal. Their recombination current is much higher than expected for the given lifetime and they show an ideality factor larger than 2 at relative low voltages. One way to explain the high ideality factor is high series resistance or shunt resistance due to the indium contact soldered onto lightly doped Si.

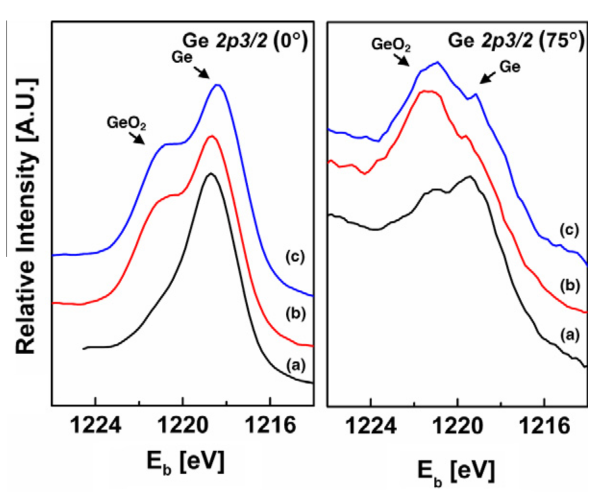

Fig. 1. ARXPS analysis of the Ge 3p3/2 shape profile of activated Ge surface: (a) cleaned in an SC1-equivalent solution, (b) SC1 + oxygen (O_2) radical 10 min exposure, and (c) SC1 + nitrogen (N_2) radical 10 min exposure.

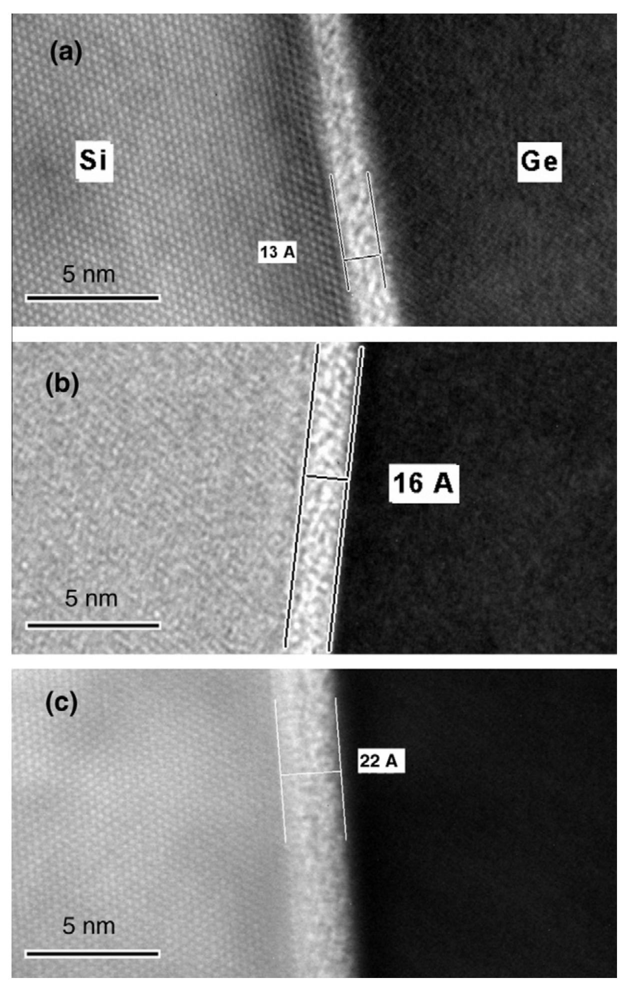

Fig. 2. HR-TEM micrographs of buried interface after anneal: (a) cleaned in an SC1-equivalent solution, (b) SC1 + O_2 radical 10 min exposure, and (c) SC1 + N_2 radical 10 min exposure.