Microstructural and surface characterization of thin gold films on n-Ge (111)

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ABSTRACT

Thin gold films were fabricated by vacuum resistive deposition on the n-Ge (111) wafers. The films were annealed between 300 and 600 °C. These resulting thin films were then characterised using scanning electron microscopy (field emission and back-scattering modes), Rutherford back scattering spectroscopy and time of flight secondary ion mass spectroscopy (TOF-SIMS). For temperatures below the eutectic temperature the distribution of both the gold and the germanium on the surface are uniform. Above the eutectic temperature, the formation of gold rich islands on the surface of the Germanium were observed. These changes in the microstructure were found to correspond to changes in the electrical characteristics of the diodes.

1. Introduction

Germanium was the preferred host for many of the early studies on defects in semiconductors. The research was driven by the search for sensitive detectors for gamma radiation [1]. Defects and defect formation in Ge have recently generated new interest because of their potential applications. The low effective mass of holes in Ge has opened up the possibility of using Ge in ultrafast complimentary metal-oxide-semiconductor devices [2]. This, in turn, has sparked renewed interest in the properties of defects in Ge because defects ultimately determine the performance of devices. Germanium-on-insulator (GeOI), which combines high mobility of charge carriers with the advantage of a silicon-on-insulator (SOI) structure, is an attractive integration platform for the future integrated circuit technology. Also, due to its low lattice mismatch with GaAs, III–V compound transistors as well as opto-electronic functions can be integrated on GeOI [3].

To exploit the advantages of germanium, an appropriate contact technology will have to be developed. Analogous to the silicon-based technology, where metal silicides are used to obtain low-resistance contacts, contacts made of metal germanides could exhibit low sheet and contact resistance, good stability after heat treatment and could be formed by means of simple technological processes like thermal evaporation at low temperatures. Data concerning the behaviour of metal thin films on germanium upon thermal treatment is relatively scarce. The thin film reactions of 20 transition metals, excluding gold, with germanium substrates have been reported [4]. It was found that among the investigated materials Ni and Pd were the most promising candidates forming low resistivity monogermanides at low temperatures. The formation of particularly NiGe contacts has been investigated in some detail [5]. Gold–germanides have also been used to form low resistivity contacts on substrates such as GaAs and SiO_2 [6,7]. In these studies it has been found that the Ge diffuses through the Au to the surface, and forms a Ge-oxide [6,7]. The focus in this paper is the effect of thermal treatment on thin gold films in n-Ge (111).

2. Experimental

A bulk-grown (111) 2-in Ge wafer doped n-type with Sb to a level of 2.5×10^{15} cm^{-3} was cut into manageable pieces (3×5 mm) and degreased in successive trichloroethylene, acetone and methanol ultrasonic baths. After a de-ionized water rinse, the samples are etched in a mixture of $1H_2O_2$ (30%): $5H_2O$ for 1 min, rinsed again in de-ionized water, and inserted into a vacuum chamber, after drying, where Au was resistively deposited on the surface. After deposition the samples were annealed in an argon atmosphere for 10 min at temperatures ranging from 300 to 600 °C. The electrical characteristics of gold-based schottky barrier diodes on Ge after annealing have been discussed elsewhere [8]. The resulting surface microstructures were examined using scanning electron microscopy (Field emission (FESEM) and backscattered SEM). Rutherford backscattering (RBS) in both the random and channeled orientations at room temperature,

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(utilizing 1.4 MeV He$^+$ ions from a 2.5 MV Van de Graaff accelerator), and Time of flight secondary ion mass spectroscopy (TOF-SIMS) were used to determine the composition and distribution of elements on the surface and into the near surface after sputtering.

3. Results

From a previous study of the electrical properties [8], a negligible change in the forward bias characteristics was observed, but a significant variation in the reverse leakage current was observed. Along with the change in I–V properties, when viewed under an optical microscope at low magnification (about 100×) there was a visible change in the morphology of the gold film from a relatively featureless surface to a more textured surface. This was observed in more detail on the FESEM images where the surface up to an annealing temperature of 300 °C was seen to be a uniform thin gold film covering the Ge surface, Fig. 1(a). However, after annealing at 400 °C, particles of varying sizes were observed on the surface, Fig. 1(b). These particles had a lamella/spongelike structure. Similar structures were observed after annealing at 500 and 600 °C, however, after 500 °C annealing a darker phase was observed in the FESEM images, Fig. 1(c) and after 600 °C voids (which could be attributed to thermal etching) had developed on the surface, Fig. 1(d).

TOF-SIMS results of the Au–Ge surfaces after annealing at the different temperatures are summarised in the compositional images shown in Fig. 2. These images show changes in composition which can be correlated with the change in morphology seen in Fig. 1. After annealing at 300 °C there is a uniform coverage of Au across the surface, but there is also a significant amount of Ge detectable across the surface, Fig. 2(a). This is consistent with previous studies [6,7] where it was found that Ge diffused through

a Au layer to locate on the surface, even at temperatures as low as room temperature. As the temperature increased, the distribution of the elements on the surface changed significantly as seen in Fig. 2(b–d). The particles observed in these figures can be seen to be gold rich. The particles observed in the FESEM were also analysed in a conventional SEM equipped with an EDX facility, and the particles were confirmed to be Au-rich particles as observed in the TOF-SIMS images.

From RBS studies after annealing at various temperatures [8], an abrupt change in the Au and Ge concentrations on the surface was observed. In the same temperature range, a eutectic point exists in the Au–Ge system (361 °C and 28at% Ge) [9]. The solid solubility of Ge in Au is 3.1at%, whereas that of Au in Ge is very low, $<10^{-5}$at% [10]. Fig. 3 shows the normalized backscattering yield of Au and Ge as a function of annealing temperature, and it is clear that a sharp increase in the germanium concentration is accompanied by a sharp decrease in the gold concentration between 360 and 361 °C. This coincides with the eutectic temperature (361 °C), but the Ge concentration is much higher than expected for a Ge in Au solid solution. This high Ge concentration can be due to the diffusion of Ge through the gold film to the surface. This has also been previously observed (even at room temperature) [6,7], however the concentration of the Ge on the surface is still higher than those reported by Zhang et al. [6].

Combining the microstructural images, TOF-SIMS compositional images and the RBS results, higher than expected Ge concentration is likely to be due to the germanium surface being exposed during the formation of the gold rich islands at the eutectic temperature and above. The formation of gold islands have also been reported to form on (100) Si during annealing due to the high surface tension of gold, and with longer annealing times, the formation of gold silicide has been reported [11].
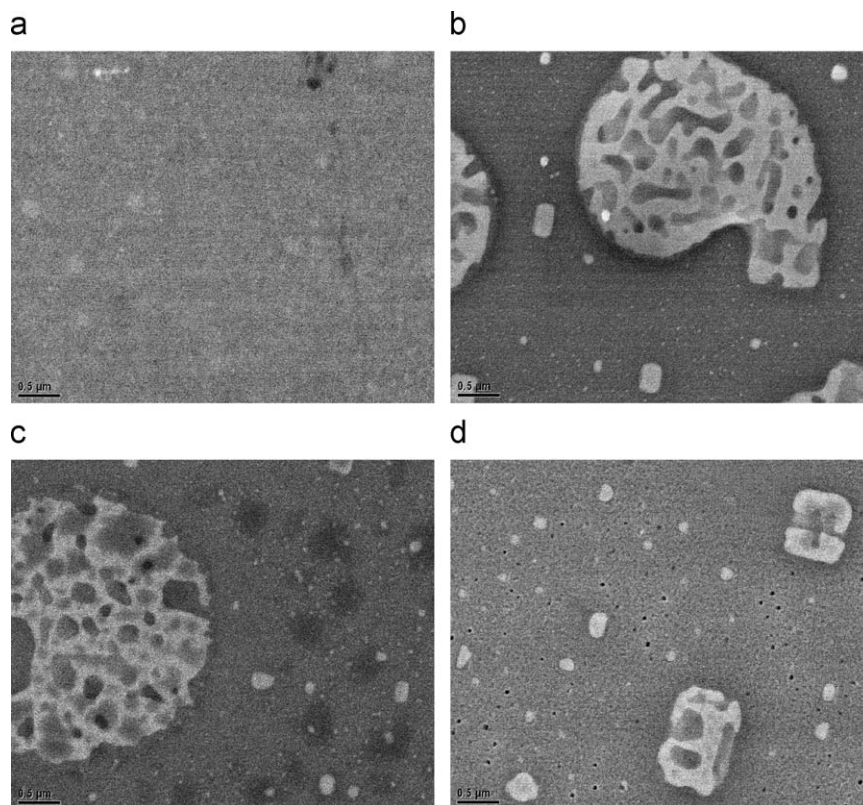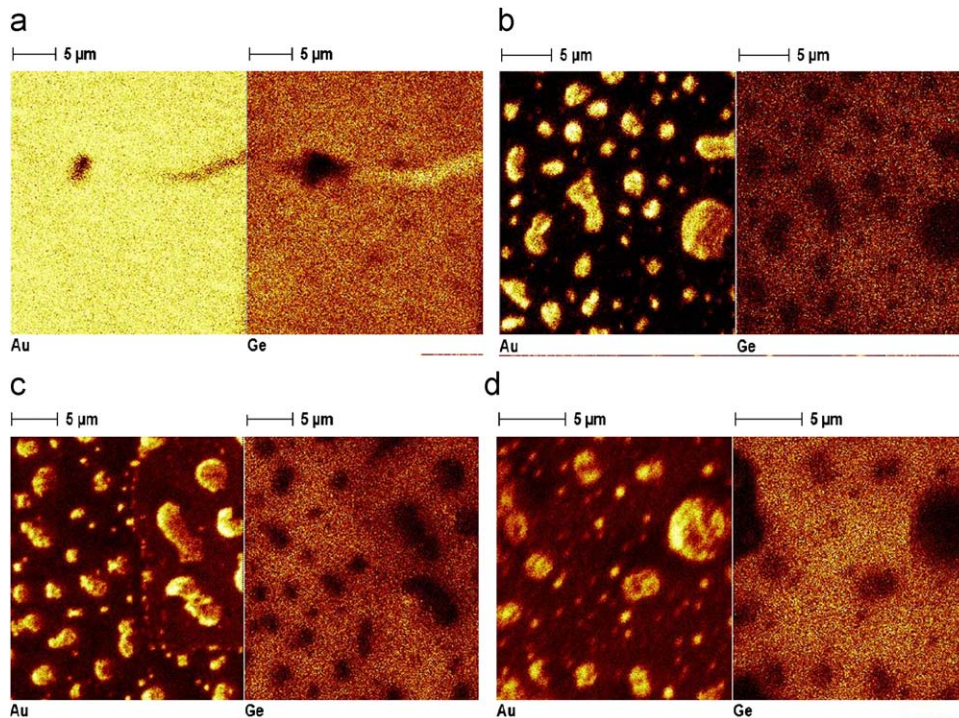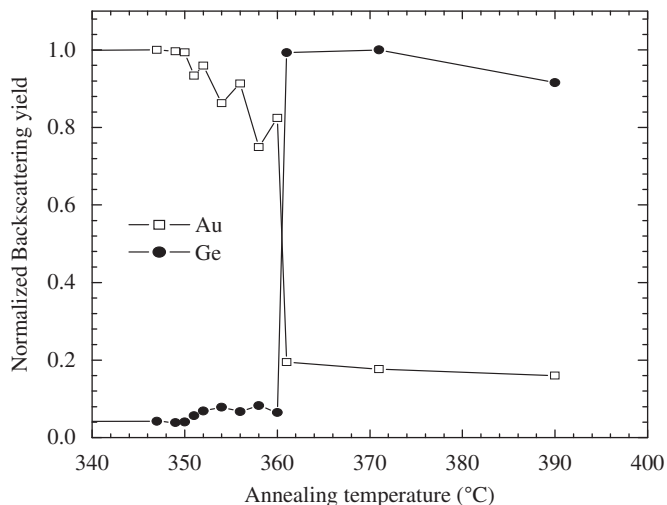

Fig. 1. FESEM images of the Au on Ge (111) surfaces after etching at (a) 300 °C, (b) 400 °C, (c) 500 °C and (d) 600 °C. Scale bar=0.5 μm.

Fig. 2. TOF-SIMS compositional images indicating Au and Ge distribution after (a) 300 °C, (b) 400 °C, (c) 500 °C and (d) 600 °C.

Fig. 3. Normalized backscattering yield of Au and Ge versus annealing temperature for 30 nm thick Au-layers deposited on Ge (1 1 1) and thermally treated in a Ar-atmosphere. For thicker Au-layers (up to 100 nm) a similar trend was observed.

4. Conclusions

For temperatures below the eutectic temperature of 361 °C, there is significant diffusion of Ge through the gold film, but the distribution of both the gold and the germanium on the surface are uniform. Above the eutectic temperature, the formation of gold rich islands on the surface of the Germanium were observed. The formation of a gold–germanide phase could occur, but this has not been quantitatively confirmed. However, it was observed that significant amounts of germanium are present on the surface at temperatures higher than the eutectic temperature. Taking into account the microstructural evidence, it is concluded that this is mainly due to the germanium surface being exposed during the formation of the gold-rich islands on the surface.

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