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Formation and texture of palladium germanides studied by *in situ* X-ray diffraction and pole figure measurements

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ABSTRACT

The solid state reaction between 30 nm Pd films and various Ge substrates (Ge(100), Ge(111), polycrystalline Ge and amorphous Ge) was studied by means of *in situ* X-ray diffraction and *in situ* sheet resistance measurements. The reported phase sequence of Pd_2Ge followed by PdGe was verified on all substrates. The texture of the germanides was analysed by pole figure measurements on samples quenched in the Pd_2Ge and in the PdGe phase on both Ge(100) and (111) substrates. We report an epitaxial growth of Pd_2Ge on Ge(111) and on Ge(100). The formed PdGe has an axiotaxial alignment on Ge(111). On Ge(100), the axiotaxial texture is observed together with a fibre texture. The higher formation temperature of PdGe on Ge(111) could be related to the epitaxial alignment of the Pd_2Ge parent phase on Ge(111).

1. Introduction

Over the past decades, silicides were extensively studied in view of their important role as a contacting material in micro-electronics [1–3]. For future semiconductor technologies, germanium is considered as a potential alternative to silicon because of its higher electron mobility. In analogy with silicides, the self-aligned formation of germanides can be expected to play an important role in Ge-based technologies. In a recent study, Gaudet et al. [4] identified NiGe and PdGe as the most promising candidates for source-drain contact applications on Ge, because of their low temperature of formation, low resistivity (20–30 μΩ-cm) and stability over a relatively wide temperature range. While the solid-state reaction between Ni and Ge has been studied in quite some detail [5–8], relatively few reports can be found in literature concerning the formation and properties of Pd germanides. Heating of Pd films on Ge was reported to result in the formation of a hexagonal Pd_2Ge phase, followed by the formation of orthorhombic PdGe at higher temperatures [4,9–11]. The hexagonal Pd_2Ge phase was reported to grow epitaxially on Ge(111) substrates [10–12]. In this work, we report a systematic study of the solid-state reaction between 30 nm thick Pd films and Ge(100), Ge(111), polycrystalline Ge and amorphous Ge substrates. The effect of the crystalline nature and orientation of the substrate on germanide formation were studied by *in situ* X-ray diffraction (XRD) and *in situ* sheet resistance measurements. Preferential grain orientation in the resulting Pd_2Ge and PdGe layers was studied by pole figure measurements, and several epitaxial and axiotaxial texture components could be identified.

2. Experimental details

To investigate the thin film reaction between Pd and Ge, four different Ge substrates were selected: monocrystalline Ge(100) and Ge(111), polycrystalline Ge and amorphous Ge. The polycrystalline and amorphous Ge substrates where formed by depositing 300 nm Ge by means of respectively chemical-vapour deposition (at 400 °C) and thermal evaporation on SiO_2 wafers. Prior to the deposition of Pd, all wafers received a short 20 s HF (2%) dip. 30 nm of Pd was sputter deposited in an Ar atmosphere with a pressure of $5 \cdot 10^{-1}$ Pa after a base pressure of 10^{-4} Pa had been reached in the physical-vapour deposition system.

Information about the phase formation was extracted from *in situ* sheet resistance measurements and *in situ* X-ray diffraction measurements at the X20C beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The energy of the X-rays was selected at 6.9 keV ($\lambda = 0.180$ nm) with an energy resolution of 1.5% by a multilayer monochromator. The diffracted X-rays were collected with a linear detector covering about 14° in 2θ at a rate of one diffraction pattern per 0.5 s while heating the sample. The *in situ* XRD data was acquired while heating the sample in a purified He atmosphere from room temperature to 900 °C at a constant rate of 3 °C/s.

The texture of the germanide film was studied using XRD pole figure measurements at the X20A beamline of NSLS. Pole figures are obtained

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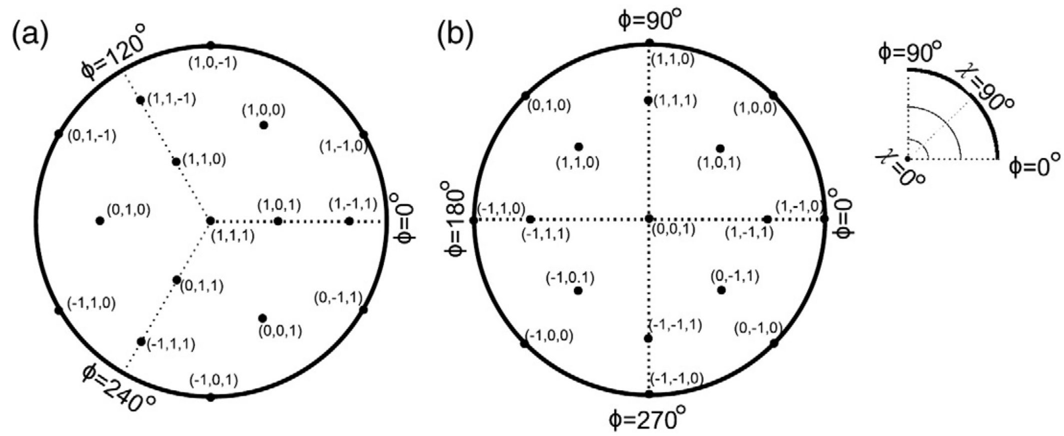

Fig. 1. Location of some of the substrate poles in the pole figures in function of χ and Φ for (a) Ge(111) and (b) Ge(100).

by measuring the diffracted intensity at a given diffraction angle 2θ, while tilting and rotating the sample over a range of angles χ and Φ using an Euler cradle [13]. The value of 2θ can be related to a specific {*hkl*} lattice plane of a certain phase, and by plotting the data as a function of angles χ and Φ for a single value of 2θ, one can then represent a statistical distribution of the preferred orientation of the corresponding {*hkl*} plane. In this work, pole figures were measured using an X-ray wavelength of $\lambda = 0.154$ nm, as selected using a Si monochromator. The diffracted X-rays were detected using a custom linear detector (8 cm Si strip detector, 640 pixels) which allows the simultaneous acquisition of pole figures covering 2θ values in a 42° range. The pole figures were acquired in steps of 0.5° in Φ and χ ($0 \leq \chi \leq 85°$ and $0 \leq \Phi \leq 90°$ for Ge(100) or $0 \leq \Phi \leq 120°$ for Ge(111)). The complete pole figures were obtained by extending the measured data to the full range $0 \leq \Phi \leq 360°$, taking into account the symmetry of the substrate. The samples were positioned so that the Ge poles are at the Φ and χ locations as shown in Fig. 1. A more detailed description of the pole figure measurements and their analysis can be found in our earlier work describing the formation and texture of NiGe [8], NiSi [14,15], α-$FeSi_2$ [16], $CoSi_2$ [17] and Co germanides [18].

3. Experimental results and discussion

3.1. Phase formation

To study the solid-state reaction, *in situ* XRD measurements were performed while annealing the samples in a He ambient to 900 °C at a fixed rate of 3 °C/s. The resulting data for a 30 nm thick Pd layer on polycrystalline Ge are shown in Fig. 2b and c. The measured diffracted intensity is displayed as a function of temperature in a contour plot using a logarithmic grey scale. The *in situ* sheet resistance data, which was acquired simultaneously with the XRD data, is shown in Fig. 2(a). The XRD data allows a straightforward determination of the sequence and the temperatures at which different germanide phases are formed during the solid-state reaction. At room temperature, the Pd(111) peak is observed at 47°, together with the Ge(311) peak near 63° 2θ. The Ge(311) peak remains present during the entire heat treatment, which indicates the relative abundance of Ge in this sample. At a temperature of 200 °C, the Pd peak starts to decrease in intensity and hexagonal Pd_2Ge (a = 0.6712 nm and c = 0.3408 nm [19]) starts to form as indicated by the appearance of the $Pd_2Ge(11\bar{2}1)$ peak near 44° and $Pd_2Ge(0002)$ peak near 63°. The Pd_2Ge layer continues to grow until the entire Pd film is consumed. Around 300 °C, Pd_2Ge starts to consume Ge to form orthorhombic PdGe (a = 0.6259 nm, b = 0.5782 nm and c = 0.3481 nm [20]), as indicated by the appearance of the PdGe(101), (210), (111), (211), (301) and (002) peaks at 35, 38, 39, 49, 60 and 62°, respectively. According to the XRD data, this PdGe remains stable until its melting temperature near 725 °C.

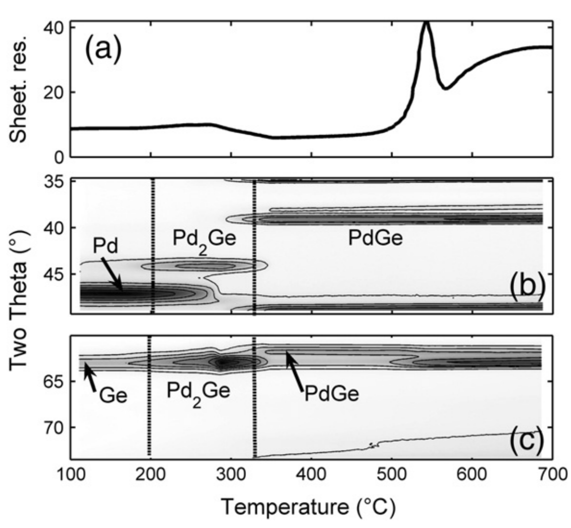

Fig. 2. *In situ* sheet resistance (a) and XRD (b, c) results during compound formation for a 30 nm Pd film on a poly-Ge wafer.

Additional information regarding the phase formation can be obtained from the simultaneous *in situ* sheet resistance measurement. By comparing Fig. 2(a) with (b) and (c), the small increase in sheet resistance starting at 200 °C can be related to the formation of the Pd_2Ge phase while the subsequent drop in sheet resistance at around 300 °C correlates with the formation of PdGe. This behaviour can be explained as PdGe is a low resistivity phase with a thickness that exceeds that of the original Pd film. Assuming that the entire 30 nm Pd film reacted and formed PdGe, the thickness of the resulting PdGe film equals 64 nm. This means that the measured sheet resistance of $5.9\Omega/\square$ corresponds to a resistivity value of $38.4\mu\Omega$-cm which is slightly higher than the value of $30\mu\Omega$-cm previously reported by Gaudet et al. [4]. Around 500 °C, a steep increase in the sheet resistance can be observed, which cannot be explained by a corresponding phase transformation of the Pd germanide. This increase in sheet resistance is an indication of agglomeration whereby the Ge and germanide mixes [4].

In situ XRD experiments were also performed during the solid state reaction of Pd with a-Ge-, Ge(100)- and Ge(111)-substrates, as shown in Fig. 3. The measurements on Ge(100) and a-Ge are very similar to the poly-Ge substrate, with limited differences in the peak intensities and the formation temperatures of the different germanide phases. It is clear that the same phase sequence of Pd_2Ge followed by PdGe occurs on Ge(100), a-Ge and poly-Ge substrates. However, the Pd_2Ge phase is not observed in the *in situ* XRD-measurement on Ge(111). To investigate this further, XRD pole figures were measured on a sample quenched at 334 °C on the Ge(111) substrate. While a regular $\theta/2\theta$