Microelectronic Engineering 87 (2010) 258–262

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

In situ X-ray diffraction study of thin film Ir/Si solid state reactions

W. Knaepen [a,*], J. Demeulemeester [b], D. Deduytsche [a], J.L. Jordan-Sweet [c], A. Vantomme [b], R.L. Van Meirhaeghe [a], C. Detavernier [a], C. Lavoie [c]

[a] Department of Solid-State Sciences, Ghent University, 9000 Gent, Belgium
[b] Instituut voor Kern- en Stralingsfysica and INPAC, K.U.Leuven, B-3001 Leuven, Belgium
[c] IBM T.J. Watson Research Center, Yorktown, USA

ARTICLE INFO

Article history:
Received 17 April 2009
Accepted 7 June 2009
Available online 12 June 2009

Keywords:
Ir
Si
NiSi
XRD

ABSTRACT

The solid state reaction between a thin (30 nm) Ir film and different Si substrates (*p*-type Si(1 0 0), *n*- and *p*-type Si(1 1 1), silicon on insulator (SOI) and polycrystalline Si) was studied using a combination of in situ X-ray diffraction (XRD), in situ sheet resistance and laser light scattering measurements. No significant influence of either the dopants or the substrate orientation was detected as a phase formation sequence of IrSi, Ir_3Si_4, Ir_3Si_5 and $IrSi_3$ was found for all samples. The presence of a thin (<4 nm) amorphous IrSi film at room temperature and its subsequent crystallization could be deduced from the appearance of a broad semi-amorphous diffraction peak in the XRD spectrum around 400 °C. The results were verified using ex situ Rutherford Backscattering Spectroscopy, Scanning Electron Microscopy and 4-point probe measurements on quenched samples. The activation energy of the crystallization process and the silicide growth was determined using a Kissinger analysis on ramp anneals with different ramp rates. In addition, the influence of up to 25 volumetric % (20.5 atomic %) of Ir to the silicide formation in the Ni/Si system was studied on SOI and polycrystalline Si substrates. In the presence of Ir, the temperature range over which the low resistivity NiSi exists, is reduced both through an increase in formation temperature and an earlier consumption by the formation of $NiSi_2$. After the heat treatment, a continuous distribution of Ir throughout the $NiSi_2$ phase was detected using X-ray photoelectron spectroscopy depth profiling. A low sheet resistance of $< 20\ \Omega/\square$ was maintained on both substrates up to 900 °C.

1. Introduction

The continued downscaling in complementary-metal-oxide-semiconductor (CMOS) technology leads to an increasing influence of Source/Drain series resistances on transistor performance. In order to address some of the challenges this creates for contact materials, one alternative is to use silicide contacts that display a very low Schottky barrier to electrons or holes depending on the dopant of the Si substrate. Iridium silicides are interesting contact materials for *p*-type Si substrates as they display the lowest barrier to holes reported in literature (about 0.15 eV) [1,2]. Because of this very low Schottky barrier, Ir is also considered as an alloying element in fully silicided gates (FUSI) applications where its low Schottky barrier can be used for band gap modulation of NiSi.

However, the use of Ir-silicides in these applications requires foremost a thorough understanding of the Ir/Si solid state reactions. On Si(1 0 0) and Si(1 1 1), three successive phases have been observed during the Ir silicidation process: IrSi, $IrSi_x$ and $IrSi_3$ [3–7]. The exact stoichiometry of the $IrSi_x$ phase is still subject to debate with $x = 1.60–1.75$ but it is most often identified as monoclinic Ir_3Si_5. As is typically observed with sputtered metals on Si substrates, the metal-Si intermixing is already started by the energetic deposition process as a very thin film of amorphous IrSi (<4 nm) is detected at the Ir/Si interface after deposition [8]. The presence of such a thin amorphous layer between 2 crystalline phases is a common phenomenon in thin film reactions and can be attributed first to the high energy Ir atoms produced for the deposition but also to a solid state amorphization process which is driven by a negative enthalpy of mixing between Ir and Si [9–11].

In this paper, the solid state reaction between a thin (30 nm) Ir film and different Si substrates was studied using a combination of in situ X-ray diffraction (XRD), in situ sheet resistance and laser light scattering (LLS) measurements. The formation of IrSi, Ir_3Si_4, Ir_3Si_5 and $IrSi_3$ was detected on all substrates. The formation kinetics of these silicides were studied using a Kissinger analysis on ramp anneals with various fixed ramp rates. In addition, the in situ setup was used to study the phase formation in 10 nm Ni/Ir alloys on SOI and poly-Si substrates. The Ir addition delayed the NiSi formation while the formation of $NiSi_2$ was enhanced.

---

[*] Corresponding author.
E-mail address: werner.knaepen@UGent.be (W. Knaepen).

doi:10.1016/j.mee.2009.06.002

2. Experimental procedures

The substrates used in this paper consist of HF-cleaned *p*-type (B-doped) Si(1 0 0), *p*- and *n*-type (P-doped) Si(1 1 1), (1 0 0)-oriented silicon on insulator (SOI) and polycrystalline Si (poly-Si). The doped substrates all had a resistivity in the 1–15 Ω cm range. A 30 nm Ir film was deposited on top of the substrates immediately followed by the deposition of a thin (5 nm) Si cap in order to prevent oxidation of the samples. We also prepared 10 nm Ni/Ir mixed films by codeposition on SOI and poly-Si substrates with an Ir concentration of 1, 3, 5, 10, 15, 20 and 25 volume % (0.7–20.5 atomic %). No Si cap was deposited on these samples.

The silicidation process was studied using the in situ XRD setup at the X20C beam line of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The samples were heated from 100 °C to 1200 °C in a purified He atmosphere using ramp anneals at a fixed rate of 0.3, 1, 3, 9 and 27 °C/s. In addition to the XRD spectra, the in situ setup also provided information about the resistivity and the surface roughness of the films through simultaneous acquisition of sheet resistance and laser light scattering (LLS) measurements.

The compositional depth profile of the elements in the samples was studied using ex situ Rutherford Backscattering Spectroscopy (RBS) or X-ray photoelectron spectroscopy (XPS) depth profiling. The RBS spectra were acquired using a collimated 1.57 MeV He+ beam (backscattering angle 167.6°).

3. Results

3.1. Phase formation in the Ir/Si system

The solid state reaction of the thin film Ir/Si system was identified by combining in situ XRD, sheet resistance and LLS measurements. Typical in situ results are shown in Fig. 1 for the case of a 30 nm Ir film on (1 0 0)-oriented SOI using 3 °C/s ramp anneals. In Fig. 1a, the measured sheet resistance and LLS signals are shown as a function of temperature. The corresponding XRD patterns are displayed in Fig. 1b–d with the use of a logarithmic gray scale.

The diffraction peak around 48° which is present at the start of the measurement can be identified as the Ir(1 1 1) peak. At 410 °C, a broad diffraction peak appears around 36° which indicates the growth of a crystalline Ir_xSi_y phase. The identification of this phase is not straightforward as the sole diffraction peak can be linked to a variety of possible phases: Ir_2Si(1 1 1), hexagonal-IrSi(1 0 1) or orthorhombic IrSi(0 1 1). However, the combination of the low intensity of the peak and its broad semi-amorphous nature suggests that this peak is rather caused by the crystallization of a small interlayer than by a silicidation process in which the entire Ir film is involved. This is supported by the fact that the formation of this phase has no effect on the intensity of the Ir(1 1 1) peak which remains stable up to 660 °C. At this temperature, the entire Ir film is transformed into the orthorhombic IrSi phase as indicated by the appearance of its diffraction peaks around, respectively, 25, 34, 36, 51, 52, 54, 55 and 62° 2θ. Near 705 °C, the IrSi peaks disappear and the formation of two different phases can be detected: the Ir_3Si_4 phase from its (4 0 1) diffraction peak at 28° and the Ir_3Si_5 phase from the peaks near 23, 30, 32, 33, 34, 43, 52, 55, 56 and 59°. Based on the in situ XRD data, the two phases grow simultaneously up to 720 °C at which point the IrSi film is completely consumed. A final transformation into $IrSi_3$ starts around 1080 °C, as is evidenced by the appearance of its diffraction peaks around 27, 32, 42, 49, 56 and 59°. On the SOI substrate, this transformation is not complete as diffraction peaks of Ir_3Si_5 can be detected up to 1200 °C with a lower intensity. This behavior is expected as the complete transformation of a 30 nm Ir film into $IrSi_3$ requires about 143 nm of Si and only 100 nm of Si is available.

Similar in situ XRD measurements were performed for a 30 nm Ir film on *p*-type Si(1 0 0), *n*- and *p*-type Si(1 1 1) and poly-Si (Fig. 2). No significant difference between the XRD patterns on the different substrates was observed which may indicate that the phase formation is independent of the substrate orientation or dopant type. The only exception is the lower formation temperature of the $IrSi_3$ phase on poly-Si which already starts around 1050 °C.

The evolution of the sheet resistance as a function of temperature was followed in realtime for the SOI and poly-Si substrates. As can be seen in Fig. 1a, the sheet resistance is unaffected by the formation of the Ir_xSi_y phase and increases gradually during the formation of the IrSi phase. The sheet resistance of the subsequent silicides could not be determined as the Ir_3Si_4 formation increased the sheet resistance of the samples beyond the detection range of the in situ technique. However, the sheet resistance of all silicides was determined using ex situ 4-point probe measurements on quenched samples (Table 1). These results allowed us to determine the resistivity of Ir, IrSi, Ir_3Si_5 and $IrSi_3$ while an estimation of the resistivity of the entire silicide film was found for Ir_xSi_y and Ir_3Si_4 by assuming that the Ir film is completely transformed into the dominant silicide phase.

Information about the surface roughness was obtained from the LLS signal in Fig. 1a. Based on this signal, formation of the IrSi, Ir_3Si_4 and Ir_3Si_5 phases causes a small increase in the surface roughness while the $IrSi_3$ formation induces severe roughening of the surface.

Ex situ RBS analysis was performed on samples quenched at RT, 410, 600, 700, 720, 950 and 1100 °C to determine the stoichiometry of the Ir-silicides (Fig. 3). These RBS spectra can be understood by realizing that the backscattering yield is a measure for the Ir

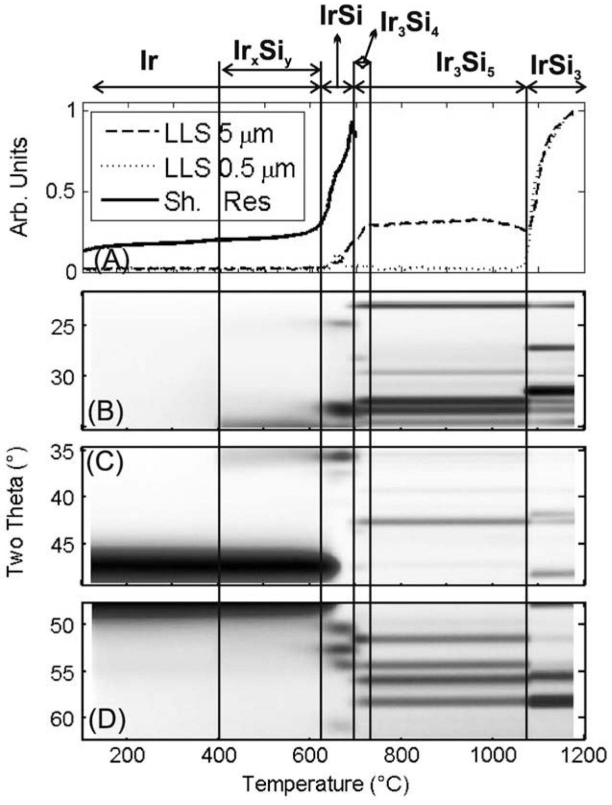

Fig. 1. In situ XRD, LLS and sheet resistance results obtained for a 30 nm Ir film on SOI using 3 °C/s ramp anneals.