Applied Surface Science 256 (2009) 1244–1248

Contents lists available at ScienceDirect

Applied Surface Science

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

Iron disilicide formation by Au–Si eutectic reaction on Si substrate

Kensuke Akiyama [a,*], Satoru Kaneko [a], Kazuya Yokomizo [b], Masaru Itakura [b]

[a] Kanagawa Industrial Technology Center, 705-1 Shimoimaizumi, Ebina-shi, Kanagawa 243-0435, Japan
[b] Department of Applied Science for Electronics and Materials, Kyushu University, 6-1 Kasuga, Fukuoka 816-8580, Japan

ARTICLE INFO

Article history:
Available online 13 June 2009

PACS:
81.05.Je
81.10.Bk
81.40.−z

Keywords:
Iron disilicide
Crystal growth
Microstructure

ABSTRACT

We have investigated the growth of iron disilicide on Au-coated Si(0 0 1) substrates and its photoluminescence behaviour. X-ray diffraction, scanning electron microscopy, and transmission electron microscopy observations revealed that the Si surface above 380 °C was melted as a result of the Au–Si eutectic reaction and that coarse island disilicide grains with sizes of several micrometres were formed on the Si surface. The full width at half maximum of 0.056° on the rocking curve of α-$FeSi_2$ *004* was observed on the sample deposited at 800 °C, and indicated the high crystal quality in perfection of orientation. The photoluminescence spectrum of β-$FeSi_2$ grains, which were deposited at 750 °C, was observed. The melted Si surface contributed to the improved crystallinity of α-$FeSi_2$ and β-$FeSi_2$.

1. Introduction

There are two kinds of iron disilicide phases in the phase diagram, i.e., α-$FeSi_2$ and β-$FeSi_2$. The α-$FeSi_2$ is a metallic phase that is thermally stable above 937 °C, and β-$FeSi_2$ is a semiconducting silicide. The photoluminescence (PL) at 1.55 μm from semiconducting β-$FeSi_2$ has attracted interest for silicon-based optoelectronic applications [1] and has been reported in various reports [2–4]. Moreover, its high optical absorption coefficient (higher than 10^5 cm^{-1} above 1.0 eV) can be advantage of using in photovoltaic devices [5]. Most β-$FeSi_2$ samples have been annealed at 800–900 °C for 2–40 h to enhance the PL intensity and photovoltaic properties [6–8]. It has been suggested that the enhancement of those optical properties by the post-annealing contributes to the decrease in the density of non-radiative centres in β-$FeSi_2$ crystal [9,10]. Thus, decreasing these crystal defects during β-$FeSi_2$ film deposition leads to sufficient optical properties without post-annealing.

In this study, we report a unique method of fabricating iron disilicide by coating an Au layer onto Si(0 0 1) substrate. The melted Si surface resulting from the Au–Si eutectic reaction led to the growth of coarse island crystal grains with sizes of several micrometres. PL from the β-$FeSi_2$ indicates good crystal quality.

2. Experimental

A gold (Au) layer of 40 nm thick was evaporated onto Si(0 0 1) substrates at room temperature in vacuum (<5×10^{-6} Torr). Iron silicides were deposited by co-sputtering iron and silicon in an argon atmosphere at substrate temperatures between 345 and 750 °C. The chamber pressure during deposition was kept constant at 3×10^{-3} Torr, and the deposition rate was set to 1.6 nm/min with the deposition time of 45 min. A 2-in. Fe–Si alloy disk with silicon chips was used as a target. The silicon/iron atomic ratio of the films was controlled by changing the areas of the silicon chips.

The deposition rates of iron and silicon were estimated from the peak intensities of Fe Kα and Si Kα radiation in X-ray fluorescence spectra (XRF) per unit time for samples deposited on magnesia (MgO) substrates that were set together with Au-coated Si(0 0 1) substrates. Both XRF and Rutherford backscattering spectroscopy (RBS) were used to measure the Si/Fe atomic ratio of the deposited silicides with calibration on standard samples. The Si/Fe atomic ratios for the films on Si and MgO substrates have been checked by X-ray photoelectron spectroscopy, XRF and RBS, and confirmed to be same level in the accuracy of ±2% [11]. The crystallographic structure of the deposited silicides was characterized from X-ray diffraction patterns (XRD, Philips MRD) using Cu Kα1 radiation. The cross-sections of the Si substrates and silicides were observed by scanning electron microscopy (SEM, FEI Shirion) and transmission electron microscopy (TEM, JEM-2000EX/T and TECNAI-F20 [STEM-EDS]). The specimens for TEM observation were prepared using a focused ion beam machine with a micro-sampling unit. The PL spectrum was measured using the 514.5-nm line of an argon-ion laser. The sample temperature was maintained at 10 K in a closed-

* Corresponding author. Tel.: +81 46 236 1500; fax: +81 46 236 1525.
E-mail address: akiyama@kanagawa-iri.go.jp (K. Akiyama).

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.05.168

cycle He cryostat. Luminescence was dispersed with a 1-m monochromator and detected with a liquid-nitrogen-cooled germanium pin-photodetector (Edinburgh Instruments, EI-L).

3. Results and discussion

3.1. Crystal structure of iron-silicide

XRD θ–2θ scan profiles for the silicides on Si(0 0 1) substrates with an Au layer at each deposition temperature are shown in Fig. 1. The silicon/iron atomic ratio of the deposits was confirmed to be 2. The XRD scan profile of the films at 800 °C showed diffraction peaks at $2\theta = 17.25°$, 34.87°, 53.47°, and 73.73°, as shown in Fig. 1(a), which were in agreement with the *001*, *002*, *003*, and *004* diffraction peaks, respectively, of the International Centre for Diffraction Data (ICDD) card for α-$FeSi_2$: 33-1843. These XRD results clearly showed that the metallic iron disilicide phase had (0 0 1)-preferred orientation. The full width at half maximum of the rocking curve of α-$FeSi_2$ *004* was 0.056°, indicating high perfection in the crystal orientation of the α-$FeSi_2$ phase. The XRD scan profiles of films between 380 and 750 °C additionally showed diffraction peaks at $2\theta = 29.07°$, 60.29°, and 77.43° (Fig. 1(b)–(d)), which were in agreement with the *202/220*, *404/440*, and *800* diffraction peaks, respectively, of the ICDD card for β-$FeSi_2$: 71-0642. These results indicate that those samples contained a mixture of α-$FeSi_2$ and β-$FeSi_2$ phases. As shown in Fig. 1(e), the formation of β-$FeSi_2$ single phase was observed for the sample deposited at 340 °C.

In our previous report, a single phase of β-$FeSi_2$ formed in the film deposited from gaseous phase at 750 °C [12], while the formation of α-$FeSi_2$ on Si(0 0 1) substrates by solid phase reaction between heated Si substrate and deposited iron has been reported [13,14]. Yamauchi et al. [15] have reported that the Au is effective in accelerating the α-$FeSi_2 \rightarrow$ β-$FeSi_2$ + Si eutectoid decomposition, and that the phase transformation rate was raised by 20 times with 0.2 at%–Au containing in isothermal annealing at 800 °C. However, in this work, (0 0 1)-oriented α-$FeSi_2$ phase was grown on Si(0 0 1) substrates with an Au layer, at a deposition temperature as low as 380 °C. This result does not support the effect of Au on accelerating β-$FeSi_2$ formation, but suggest the other effect of Au on iron silicide formation.

It is considered that the Au-coated Si surface transformed to the liquid phase in this deposition process, because the eutectic reaction between Au and Si occurs above 370 °C [16]. Taking account into this fact, the Au–Si liquid phase on Si(0 0 1) surface promoted the formation of (0 0 1)-oriented α-$FeSi_2$ phase. Actually, a single phase of β-$FeSi_2$ formed in the films deposited at 340 °C that is below Au–Si eutectic temperature.

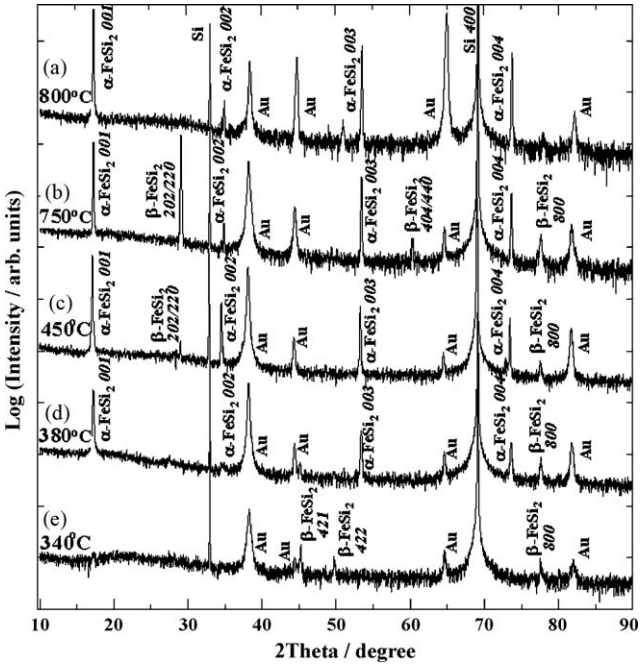

Fig. 1. (a) XRD θ–2θ scan profiles for silicides deposited on Si(0 0 1) substrates with 40-nm-thick Au layer at (a) 800, (b) 750, (c) 450, (d) 380, and (e) 340 °C.

3.2. Crystal morphology of iron-silicide

Plane-view and bird's eye-view SEM images of the iron disilicide grains are shown in Fig. 2(a) and (b), respectively. Square, trapezoid, and rod-like crystal grains with sizes of several micrometres were observed on the Si substrate surface, while a flat iron disilicide film with a thickness of 100 nm was deposited on the Si(0 0 1) substrate without an Au layer. The growth of those coarse island crystal grains indicates heterogeneous silicide-crystal nuclear generation and the growth of those nuclei. Relatively bright areas (*X* and *Y* in Fig. 2(a)) were observed in the Si surroundings of the disilicide grains, and Au was detected from these areas. We think that such an irregular distribution of Au was resultant from the melting Si surface by Au–Si eutectic reaction.

A cross-sectional TEM image of the α-$FeSi_2$ grain grown at 750 °C on Si(0 0 1) substrates with an Au layer is shown in Fig. 3(a). The α-$FeSi_2$/Si interface was formed in the interior of the Si substrates and formed a facet plane. This result indicates that the Si

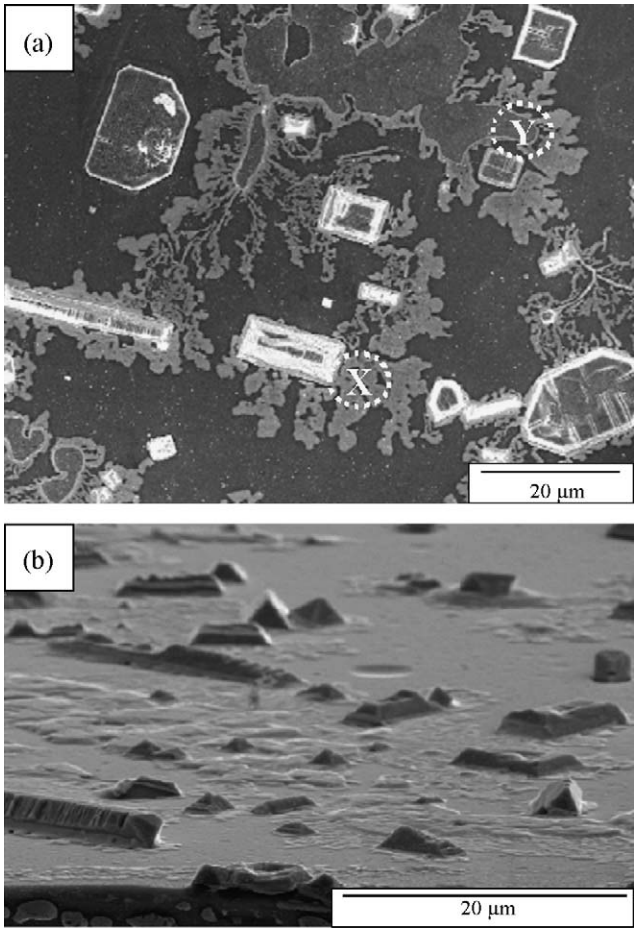

Fig. 2. (a) Plane-view and (b) bird's eye-view SEM image of silicides deposited at 750 °C on Si(0 0 1) substrates with 40-nm-thick Au layer. Au was detected from the area "*X*" and "*Y*".