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Forming the high quality $CoSi_2$ by solid phase epitaxy

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Thin films of $CoSi_2$ were grown on Si(111) by solid phase epitaxy (template technique) in UHV condition. We present a practical experimental procedure for the preparation of thin epitaxial films of cobalt silicide. Layers obtained by the deposition of metal on silicon (111) demonstrate a high -quality crystallographic structure. The state of the surface of growing layers is studied with the *in situ* combination of reflection high-energy electron diffraction (RHEED) azimuthal plots and rocking curve.

1. Introduction

From the application point of view epitaxial silicide materials form metal -semiconductor junctions which can be used as microwave diodes, infrared detectors or components of metal base transistors (MBT). In MBT the p-type base of an n-p-n bipolar transistor is replaced by a metal. This leads to a semiconductor-metal -semiconductor (SMS) structure. Epitaxial cobalt silicide seems to be appropriate for this application. Because of the small lattice mismatch (1.2%) between $CoSi_2$ and Si, cobalt silicide has been one of the most widely studied silicides. $CoSi_2$ growth by solid phase epitaxy (SPE) has been investigated for a number of years. SPE method is the simplest one and has been widely used to prepare, with success, a great number of metal silicides. Previous studies reported different aspects of Co silicide formation [1]–[4], but we have not found in the literature an accurate information about measurements of the intensity of the specularly reflected RHEED beam during SPE growth of $CoSi_2$ on Si(111).

In this paper we present a practical experimental procedure for the preparation of high-quality thin epitaxial films of cobalt silicide. The quality of these layers is confirmed by the RHEED pattern, RHEED azimuthal plots (the specular beam intensities are measured while rotating a sample around the axis perpendicular to the surface) and classic rocking curve (the intensity of one of the diffracted beams is measured for different glancing angles of the incident beam) [5], [6].

2. Experimental procedure

The $CoSi_2$ layers were grown on low resistivity (3–6 Ωcm) p-type Si(111). Mirror polished Si wafer (22×20×0.3 mm^3) was cleaned in an ultrasonic cleaner, alternatively in acetone and in methyl alcohol. Next, the sample was dipped in a dilute HF solution (HF : methyl alcohol = 1:10). After placing the wafer in the UHV chamber, a pressure of 2×10^{-10} hPa was reached. A clean, well-ordered Si(111)-(7×7) surface was prepared by flashing Si wafers. After multiple heating of the sample to about 1300 °C (3 times, each for about 3–4 s), the RHEED pattern exhibits a sharp 7×7 reconstruction of the surface. The quality of the Si(111)-(7×7) is confirmed by the RHEED pattern, RHEED azimuthal plots and rocking curve. Figure 1 presents the experimental RHEED azimuthal plots and the RHEED pattern of the Si(111)-(7×7). A CCD-based computer-controller RHEED detection and analysis system were used. The system is capable of the *in situ* measurement of time-resolved intensities of multiple diffraction beams. In order to collect the experimental data in the form of an azimuthal plot, we used a stepped motor for changing the azimuthal angle and a photodiode for detecting and recording specular beam intensity changes.

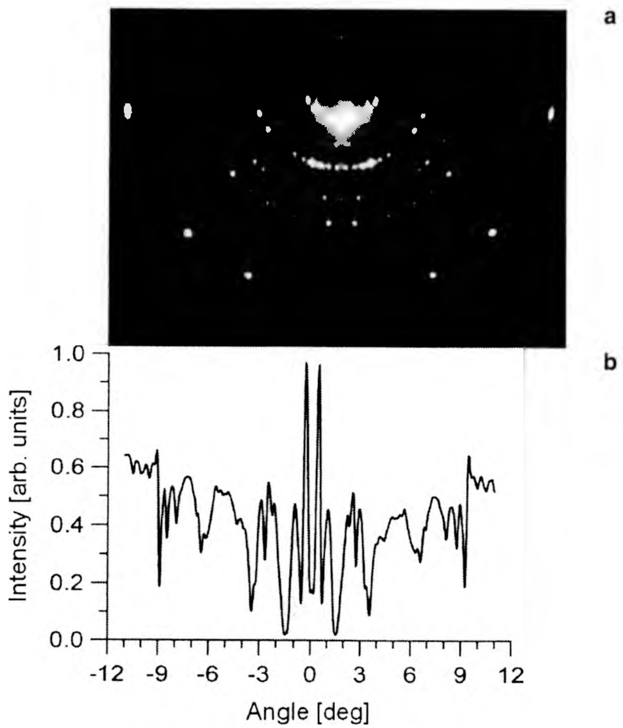

Fig. 1. RHEED pattern of Si(111)-(7×7), room temperature. Electron energy is 18 keV, azimuth of incidence [11$\bar{2}$], glancing angle is 2° (**a**). Experimental azimuthal plot of Si(111)-(7×7). The value of the azimuthal angle 0° corresponds to the azimuth [11$\bar{2}$], glancing angle is 2°. About 50 points per degree were collected during the measurements of azimuthal plots (**b**).

3. Results and discussion

During RHEED measurements the energy of the incident electron beam was 18 keV. The divergence of the incident beam (*i.e.*, the full width at the half maximum) could be estimated to be less than 0.10. Absolute values of the glancing angle and relative variations of the azimuthal angle could be determined with a precision of about ±0.2° and ±0.02°, respectively. Figure 2**a** shows an experimentally measured rocking curve for Si(111)-(7×7). The values of the glancing angles correspond to the rocking curve maxima for the 333, 444 and 555 Bragg reflections, respectively. Figure 2**b** shows a dynamically calculated one-beam rocking curve for Si(111). To the calculated one-beam rocking curve shown in Fig. 2**b** we used a computer program [6], [7], based on 1D dynamical calculations introduced by PENG, WHELAN [8], and HORIO, ICHIMIYA [9]. The calculations were carried out for Si(111) assuming the bulk -terminated surface and we took the value of 18 keV for the electron energy. We can see that the measured positions of Bragg reflections and calculated ones tally very well. The difference between them does not exceed 0.04°. For each set of experimental data, intensities were transformed according to the normalisation formula [5]–[6]:

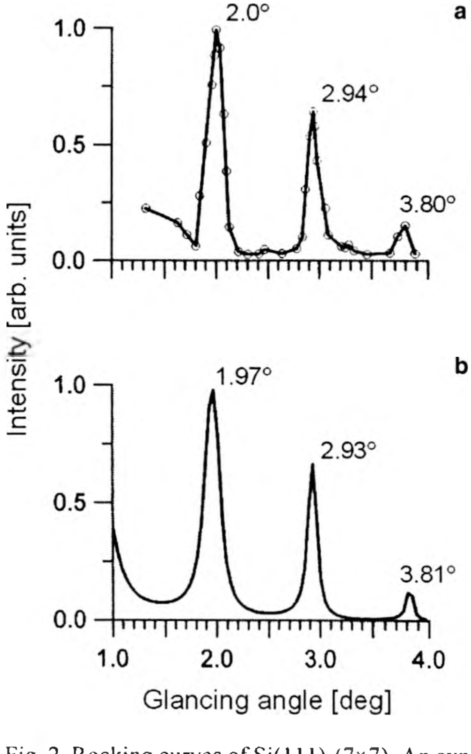

Fig. 2. Rocking curves of Si(111)-(7×7). An experiment, electron energy is 18 keV, azimuth of incidence [11$\bar{2}$], about 15 points per degree were collected during the measurements of rocking curve (**a**), one-beam calculations (**b**). The values of the glancing angles corresponding to the rocking curve maxima are shown in the figure.

$I' = (I - I_{min})/(I_{max} - I_{min})$, where I' and I are the intensities after and before the transformation, I_{min} and I_{max} are the intensity minimum and maximum in the set considered (before the transformation). The same procedure was applied to the results of the calculations.

After the preparation of the Si(111)-(7×7) substrate we started the deposition of cobalt. Using a template method (solid phase epitaxy), we prepared a layer of $CoSi_2$ with the total thickness of 20 Å. In the template technique the nucleation process is controlled by a monocrystal substrate lattice, so one can expect perfect ordering in interface silicide and silicon [1]–[4]. In the first step, to produce a silicide thin film by this technique, the amorphous cobalt layer of the thickness of about 4–5 Å on the clean silicon 7×7 was deposited at room temperature. The thickness of the film was measured with a quartz-crystal oscillator. The evaporation rate for Co was 6–10 Åmin^{-1}. Forming of $CoSi_2$ started as low as at 250 °C, when substrate was heated directly by passing dc current. During the metal deposition process the vacuum ambient pressure never exceeded 2×10^{-9} hPa, and never exceeded 5×10^{-9} hPa during the annealing process. Next, the temperature of the substrate was gradually (5–6 minutes) linearly

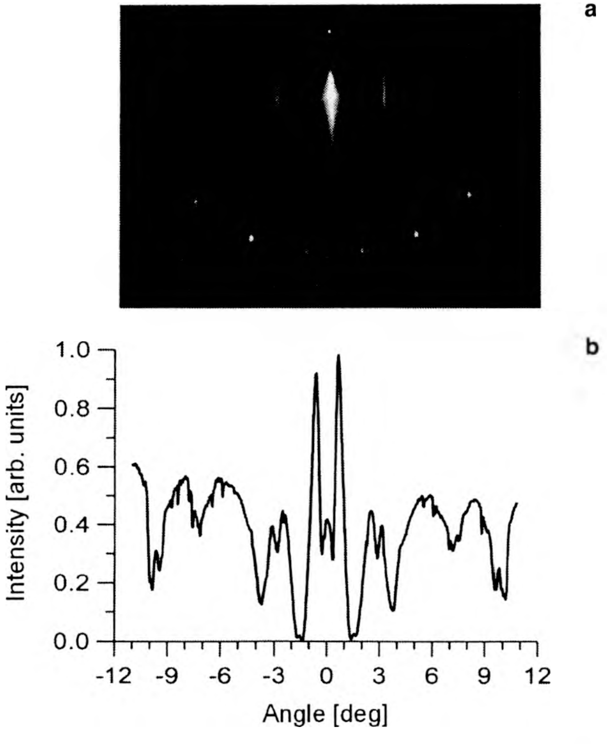

Fig. 3. RHEED pattern of $CoSi_2$ (20 Å thick) on Si(111)-(7×7), SPE method, substrate temperature is 550 °C. Electron energy is 18 keV, azimuth of incidence [11$\bar{2}$], glancing angle is 2° (a). Experimental azimuthal plot of $CoSi_2$ (20 Å thick) on Si(111)-(7×7). The value of the azimuthal angle 0° corresponds to the azimuth [11$\bar{2}$], glancing angle is 2°, silicide layers prepared by SPE. About 50 points per degree were collected during the measurements of azimuthal plots.

increased to about 550 °C to form a very good crystallographic structure of $CoSi_2$/Si(111). The quality of the structure was examined *in situ* by RHEED pattern and azimuthal plots measurements.

A typical result of the RHEED specular-beam-intensity measured for the $CoSi_2$ films on Si(111)-(7×7) surface at 550 °C in the [11$\bar{2}$] direction and for the glancing angle equal to 2±0.03° is shown in Fig. 3**a**. The value of the glancing angle corresponds to the 333 Bragg reflection for Si(111), and has been determined both numerically and

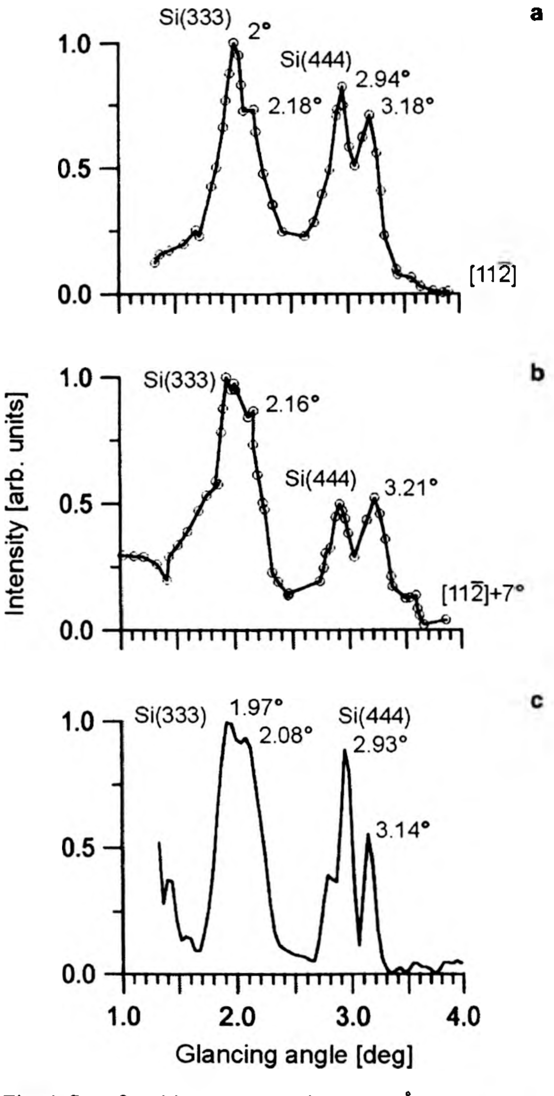

Fig. 4. Set of rocking curves of $CoSi_2$ (20 Å thick) on Si(111)-(7×7). An experiment, azimuth of incidence [11$\bar{2}$] (**a**), an experiment, azimuth of incidence [11$\bar{2}$] + 7° (**b**), one-beam calculations (**c**). Electron energy is 18 keV, about 16 points per degree were collected during the measurements of rocking curves. The values of the glancing angles corresponding to the rocking curve maxima are shown in the figure.

experimentally (see Fig. 2). Diffraction conditions (the 333 Brag reflection and azimuthal angle varied around [11$\bar{2}$]) were specially chosen to reduce the influence of the surface structure [6]. The RHEED pattern points to the near-perfect crystalline quality of the film, as well as the uniform surface morphology. Figure **3b** presents the experimental RHEED azimuthal plot for the cobalt silicide layers (20 Å thick) that has been formed with the SPE technique. On the RHEED pattern the fundamental lines (streaks) are very thin and Laue zone rings are also clearly visible and azimuthal plots contain much more details. In case of the formation of $CoSi_2$ layers with the SPE technique on a clean Si(111) the quality of these surface was very good. Moreover, the quality of the surface has been verified by rocking curve measurements. Figures **4a** and **b** shows experimentally measured rocking curves for $CoSi_2$ layers (20 Å thick) for the incidence along [11$\bar{2}$] and the azimuthal angle was chosen at 7° from the [11$\bar{2}$] direction. This incidence condition is called the one-beam condition [9], [10]. Under the one-beam condition, in which the azimuth of the incident beam direction is set to several degrees off a certain crystallographic direction, fast electrons are mainly affected by the averaged potential of atomic layers parallel to the surface.

In the measurements of the rocking curve from $CoSi_2$ layer, the influence of the substrate can be observed in the form of additional Bragg reflections from silicon. In Figure 4**a** it can be observed that the position of Si(333) and Si(444) tops tally with Bragg reflections from Si(111) substrate, *i.e.* for angles 2° and 2.94° (compare Fig. 2**a**). Rocking curve maxima, shown in Fig. 4**a**, referring to angles 2.18° and 3.18° come from $CoSi_2$ layers. Very similar relationships may be observed in Fig. 4**b**, where the azimuth of incidence was changed by 7° in comparison to the initial azimuth. Measured positions of Bragg reflections from $CoSi_2$ layers for different azimuths of incidence do not differ by more than 0.03°, which proves the precision of the measurements and stays within the limits of experimental error. Observation of additional Bragg reflections is feasible only when the $CoSi_2$ layer is very thin and is characterised by a very high quality.

Figure 4**c** shows a dynamically calculated one-beam rocking curve for $CoSi_2$ layers (20 Å thick). We can see that the measured positions of Bragg reflections and the calculated ones tally very well. Assuming that the results of one-beam calculations reproduce actual experimental situations, we can conclude that for a fixed, real surface we can find Bragg reflections experimentally with a precision of about ±0.1°.

4. Summary

The principal strength of this work is the high quality of the data presented. The diffraction images presented are of the highest quality, and the plots of intensity evolution are remarkable for their high signal-to-noise ratio.

The epitaxy technique of high quality in case of $CoSi_2$ layers allows to build of multilayer SMS structures. We have presented – in a very detailed way – the ways of *in situ* diagnosing, both for the quality of a substrate and for growing layers, and we have employed the reflection high energy electron diffraction technique. Simultaneous use of three RHEED techniques, *i.e.* RHEED pattern, azimuthal plots and rocking curve gives sufficient information concerning the quality of the resulting epitaxial layers.

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