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The room temperature growth of Ti on sputter-cleaned Si(1 0 0): Composition and nanostructure of the interface

A. Arranz, C. Palacio *

Departamento de Física Aplicada, Facultad de Ciencias, C-XII, Universidad Autónoma de Madrid,
Cantoblanco, 28049 Madrid, Spain

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Abstract

The formation of the interface during the deposition of titanium on sputter-cleaned Si(1 0 0) substrates has been studied at room temperature using X-ray photoelectron spectroscopy (XPS), angle resolved XPS (ARXPS), ultraviolet photoelectron spectroscopy (UPS) and ion scattering spectroscopy (ISS). The experimental results are consistent with a two-stage mechanism for Ti growth: a first stage characterized by the formation of a uniform layer ~4 monolayer (ML) thick of $TiSi_x$ ($x \approx 0.78$), followed by a second stage in which metallic Ti grows over the titanium silicide formed previously. During the second stage, metallic Ti grows according to a Stranski–Krastanov mechanism, with the formation of a Ti monolayer followed by the growth of metallic titanium islands with an average thickness of 7 ML. The formation of a titanium silicide during the first stage of growth, involves charge transfer from Ti to Si.

Keywords: Silicides; Metal–semiconductor interfaces; Surface chemical reaction; Photoelectron spectroscopy; Low energy ion scattering

1. Introduction

During the past two decades, great efforts have been made in the study of metal/silicon interfaces due to their growing demand in microelectronic technology [1–18]. In particular, the solid-state reaction taking place at the Ti/Si interface upon annealing has been extensively studied due to the suitability of the titanium disilicide phase, C54-$TiSi_2$, for low-resistivity contacts in microelectronic devices [6–18]. TiSi [8,11] or Ti_5Si_3 [14,15] phases have been reported as the first products at the Ti/Si interface upon annealing at ~400–500 °C, and the most stable silicide, C54-$TiSi_2$, as the final product at higher temperatures (~700 °C) [14,15]. It should be pointed out that

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* Corresponding author. Tel.: +34 91 497 5266; fax: +34 91 497 4949.
E-mail address: carlos.palacio@uam.es (C. Palacio).

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at room temperature (RT) some intermixing is produced [9–17], playing an important role in further silicide formation by solid-state reaction at higher temperatures. However, the RT Ti/Si interface reactivity has received less attention. In the 1980s some controversy occurred about the RT reaction at the Ti/Si interface and contradictory results were reported in the literature. Vähäkangas et al. [6] using Auger electron spectroscopy (AES), low-energy electron diffraction (LEED) and appearance-potential spectroscopy (APS) concluded that no intermixing exists at RT for the Ti/Si(1 0 0) and Ti/Si(1 1 1) interfaces. Similar conclusions were obtained by Taubenblatt and Helms [7] for the Ti/Si(1 0 0) interface using ultraviolet photoelectron spectroscopy (UPS), and by Butz et al. [8] for the Ti/Si(1 1 1) interface using AES and UPS. In contrast, the formation of the TiSi phase at the Ti/Si(1 1 1) interface at RT has been reported by several authors as van Loenen et al. [9] using medium energy ion scattering (MEIS), Iwami et al. [10] using electron energy loss spectroscopy (EELS), and Chambers et al. [11] and Giudice et al. [12] using X-ray photoelectron spectroscopy (XPS). Likewise, a mixture of Ti_5Si_3 and TiSi phases at RT has been reported by Wallart et al. [13] using EELS and AES. More recently, Wang and Chen [14,15,17], using reflected high energy electron diffraction (RHEED) and high resolution transmission electron microscopy (HRTEM), reported the formation of a 2 nm thick amorphous interlayer of composition close to that of TiSi due to a considerable intermixing of Ti and Si atoms during the RT Ti deposition on Si(1 0 0) and Si(1 1 1) substrates.

Nowadays the formation of a titanium silicide at the Ti/Si interface at RT is well established. However, little attention has been paid to the growth mode of Ti on Si surfaces in the above-mentioned works. Vähäkangas et al. [6] used the evolution of the Si and Ti Auger intensities to study the growth mode of Ti on Si(1 0 0) and Si(1 1 1) substrates. They found that the growth mode depends on the cleaning procedure of the Si substrate, but no intermixing was found at the Ti/Si interface. However, Wallart et al. [13] have shown that the evolution of Si and Ti Auger intensities were not consistent with a layer by layer or a three-dimensional growth of pure titanium. More recently, in a previous work carried out in our laboratory [16] using also the evolution of the Ti and Si Auger intensities during Ti deposition on Si(1 0 0) at RT, we have reported the formation of a titanium silicide during the first stage of Ti growth. Therefore, the aim of this work is to study the kinetic of growth of Ti on Si(1 0 0) substrates at RT by means of XPS, angle-resolved X-ray photoelectron spectroscopy (ARXPS), UPS and ion scattering spectroscopy (ISS), to characterize not only the composition, but also the electronic properties and, above all, the nanostructure of the Ti/Si interface. The suitability of ARXPS to study the growth mode of ultrathin films deposited in vacuum has been recently shown in other metal/substrate systems [19–21].

2. Experimental

The experiments were performed in an ultra-high vacuum (UHV) system at a base pressure better than 6×10^{-10} Torr. Si(1 0 0) single crystals (n-type, 3.5 Ω cm) manufactured by Virginia Semiconductors Inc. have been used throughout this work. They were degreased by successively boiling in carbon tetrachloride, acetone and ethanol. Then the sample was introduced into the UHV chamber. The silicon substrates were sputter-cleaned "in situ" using a low current density 3 keV Ar^+ beam rastered over an area of 1×1 cm^2 to minimize the development of ion-induced surface roughness until no impurities were detected by AES. This cleaning procedure develops small and uniform roughness (rms ∼ 0.3 nm) and induces amorphization on the silicon surface, as deduced by "ex situ" atomic force microscopy (AFM) measurements carried out using the tapping mode. Titanium was evaporated onto the Si substrates at RT by electron bombardment of a high purity Ti-wire target (99.8% purity) at constant heating power, in such a way that the amount of evaporated Ti is determined by the deposition time. According to the model of growth proposed below, the titanium deposition rate was estimated to be $\sim 8 \times 10^{14}$ atoms cm^{-2} min^{-1}. During Ti evaporation the base pressure was always kept below