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Surface Science 377–379 (1997) 266–270

surface science

Spectromicroscopy of the metastable Au/Si(111) interface studied by means of synchrotron radiation

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Received 1 August 1996; accepted for publication 15 October 1996

Abstract

The thermally agglomerated Au/Si(111) interface has been studied by means of laterally resolved photoemission by exploiting the ultra-high brightness of the ELETTRA synchrotron radiation source. The interface has been evaluated in terms of chemical maps and core level spectra acquired from selected points of the specimen surface. The variety of distinct chemical environments local to element-specific sites has thereby been clarified with an unprecedented level of resolution at both the islands and the two-dimensional superstructure terminating the Si crystal.

Keywords: Gold; Low index single crystal surfaces; Metal–semiconductor interfaces; Silicon; Synchrotron radiation photoelectron spectroscopy

1. Introduction

Since the late 1970s, massive studies have attacked the issue of semiconductor–metal interfaces from both the experimental and theoretical points of view [1]. However, few studies have focused on the evolution of these interfaces in the high temperature regime. In this connection, the case of noble metals (Cu, Ag and Au) grown on Si is of special interest. Actually, coverages of several monolayers (ML) give rise for all the three metals to agglomerated interfaces after annealing [~250°C for Cu/Si(111) [2], ~200°C for Ag/Si(111) [3] and ~350°C for Au/Si(111) [3]] with sub-micron-sized metallic islands covering the semiconductor surface which is terminated, on the uncovered flat regions, by a 1–2 monolayer (ML) thick noble-metal-related superstructure. However, despite the similar morphology, which is reminiscent of the Stranski–Krastanov growth mode, of the annealed interfaces, the atomic distribution in the space differs significantly depending on the specific noble metal species.

Here, we report a spectromicroscopy study of the thermally annealed Au/Si(111) interface by exploiting the ultra-high brightness of a new third

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PII S0039-6028(96)01380-5

generation synchrotron radiation (SR) source, i.e. ELETTRA in Trieste. Laterally resolved ($\sim$150 nm) photoemission is used to provide chemical maps and core level spectra from selected points of the specimen surface.

The Au/Si(111) interface is most probably one of the most studied metal/semiconductor contacts. In spite of the immiscibility established by bulk thermodynamics in the solid state binary alloy [4], metastable pseudo-silicides are found for ultrathin Au films deposited on top of atomically clean Si substrates [1,3,5,6]. This unexpected chemical reactivity has been demonstrated to be acting even at low temperatures. Finally, the thermally agglomerated Au/Si(111) interface can also be envisioned as a good test-bench for a comparative analysis of the potential of scanning Auger microscopy (SAM) [7] versus SR-based spectromicroscopy.

2. Experimental

All the specimen preparation was performed in a purpose built ultra high vacuum (UHV) chamber (base pressure $\approx 1\times10^{-10}$ mbar) directly connected to the spectrometer (base pressure $\approx 1\times10^{-10}$ mbar) located at the undulator beamline ESCA microscopy of the ELETTRA synchrotron radiation source.

n-type Si wafers were utilized as interface substrates. Clean and well ordered Si(111)-(7×7) surfaces were prepared by cycling Ar^+ sputtering and thermal annealing. Cleanliness was checked by Auger spectroscopy while the surface reconstruction was checked by low energy electron diffraction. Au was evaporated from an ultrapure wire wrapped around a tungsten filament while maintaining the Si substrate at room temperature. During evaporation the pressure was $<4\times10^{-10}$ mbar. The film thickness was measured by means of a quartz microbalance. The herein reported coverages are referred to the Si(111) surface atomic density ($\sim7.8\times10^{14}$ atoms/cm^2). After evaporation the interfaces were annealed at selected temperatures for $\sim$20 min. The temperature was measured with an optical pyrometer. Depending on the specific interface growth parameters (coverage and annealing temperature), $\sqrt{3}\times\sqrt{3}$ and 6×6 superstructures were observed. The data which are shown below refer to $\sim$20 ML of initial Au coverage resulting in a $\sqrt{3}\times\sqrt{3}$ pattern after annealing at $\sim$400°C.

The specimens were then transferred to the spectrometer where a Fresnel optics provides a $\sim$150 nm laterally resolved monochromatized beam ($h\nu=490$ eV). More technical details about the beamline are published in Ref. [8]. Electron energy distribution curves (EDC) were measured by means of a hemispherical analyser (angle of emission $\approx$19°) operated in the constant energy-resolution mode (overall working energy resolution $\approx$0.44 eV). The specimens are moved using piezoelectric motors so that either EDC spectra can be measured on selected points of the surface or chemical maps can be acquired by selecting an element-specific core level while scanning an appropriately chosen surface area.

After the synchrotron radiation run, a set of annealed interfaces were analysed ex situ with a scanning electron microscope (SEM) to check, with high lateral resolution ($\sim$10 nm), the specimen topography.

3. Results and discussion

The SEM images (not shown here for space limitations) gave, for all the analysed samples, similar scenarios: flat regions and micron-sized islands whose density could span the 0.4–1 μm^{-2} range, depending on the specific thermal history. Previous studies [5,7] have clarified that the islands are primarily of Au and are terminated with an ultrathin (1–2 ML) metastable pseudo-silicide film, while the flat regions are covered by $\sqrt{3}\times\sqrt{3}$R30° and 6×6 Au–Si superstructures, depending on the Au coverage. It is worth remarking that the LEED patterns are due to these ordered two-dimensional phases terminating the flat regions [1].

Fig. 1 shows a series of chemical maps obtained from the Au/Si(111) interface ($\Theta_{Au}\approx$20 ML) after annealing at $\sim$400°C. All the data presented in this paper refer to a $\sqrt{3}\times\sqrt{3}$ LEED pattern. These maps were obtained by tuning the electron spectrometer to the Si 2p and Au 4f core level emission, respectively. More precisely, the signal displayed

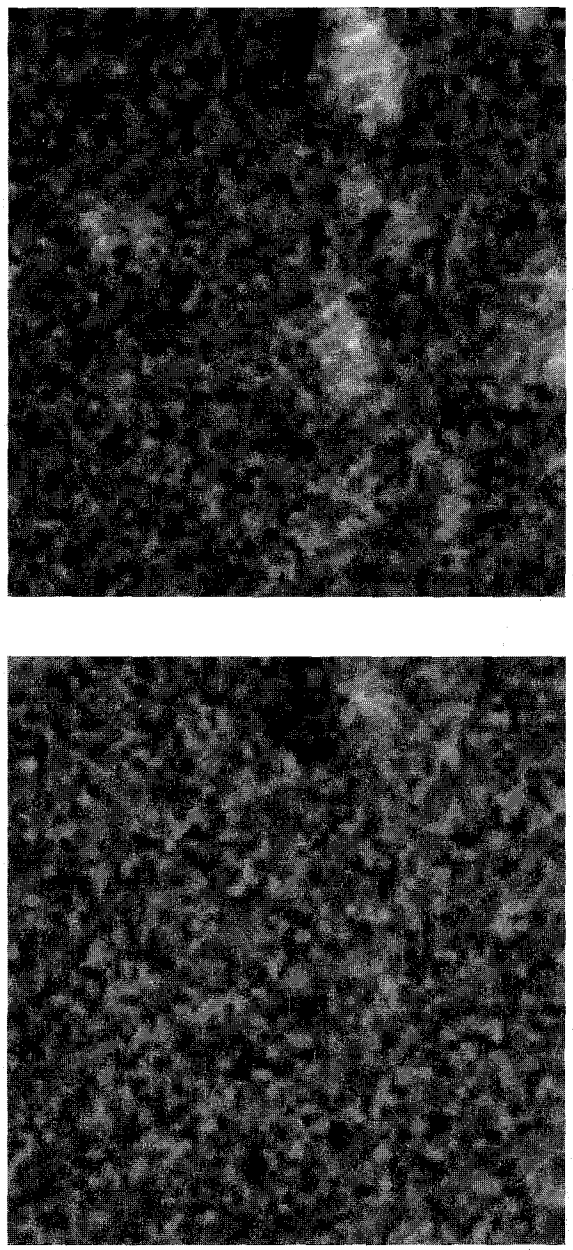

Fig. 1. Chemical maps (64×64 pixels $\times$ 0.2 μm step) obtained by tuning the electron spectrometer to the Si 2p (bottom panel) and Au 4f (top panel) core level emission, respectively. For more details, see text.

in Fig. 1 as a function of the lateral position at the specimen surface results after normalizing the core level emission to the structureless background emission located at slightly lower kinetic energies. This normalization procedure removes possible topographic effects from the maps. The colour code goes from black to white. Fig. 1 unambiguously shows that Si- and Au-related signals are found at both the flat regions and the atop layers of the agglomerated islands. These results are consistent with the chemical maps obtained by means of a scanning Auger spectrometer (lateral resolution $\approx$ 200 nm) by some authors [7] on thermally agglomerated Au/Si(111) interfaces grown on cleaved Si bars.

Fig. 2 collects a series of relevant Au 4f core level spectra. They refer to the same sample chemically mapped in Fig. 1. It is worth noting that a line shape analysis of the Si 2p core level emission yields conclusions in excellent agreement with the aforementioned Au 4f core level analysis. Si 2p photoemission profiles are not shown for space limitations; a more detailed report will be published elsewhere [9]. In particular, spectra from flat regions and islands are shown along with a reference profile from a clean thick Au film deposited onto an unreactive tantalum foil. The core level profile of the flat region is quite similar to that measured (not shown here) on the laterally homogeneous $(\sqrt{3} \times \sqrt{3})$-Au/Si(111) interface obtained by annealing a submonolayer coverage ($\theta \approx 1$ ML) evaporated onto a clean Si(111)-(7×7) substrate. We notice that the spectra of the laterally inhomogeneous interface shown in Fig. 2 are statistically representative of the associated morphology, i.e. Au 4f profiles taken on the islands are quite similar to each other as are spectra from the flat regions. A visual analysis of the Au 4f line shape reveals that the chemical environment local to the Au sites is dramatically different when comparing flat regions versus islands. Remarkably, two chemically distinct components are easily identified at the islands. To be more quantitative, the line shapes of Fig. 1 have also been best-fitted in terms of Voigt functions (also shown in Fig. 2). The basic Gaussian and Lorentzian (FWHM $\approx$ 0.31 eV) profiles as well as the asymmetry parameter α were chosen in accordance with literature data (phonon broadening and core hole lifetime) and the energy resolution of our experiment. The spin–orbit splittings and branching ratio

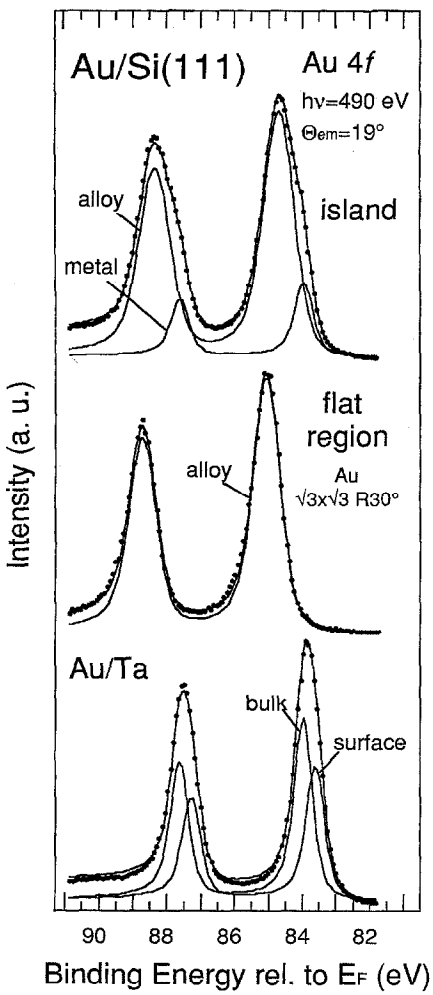

Fig. 2. Au 4f core level emission measured in the laterally resolved mode and corresponding to selected points at the specimen surface. The fit of the Au metal film is performed in terms of bulk and surface shifted components.

were also in agreement with reported results [1,6,10,11]. It is worth noticing that our best-fitting parameters are quite close to those recently reported by Yeh et al. [6] and Molodtsov et al. [11] for the Au/Si(111) interface grown at room temperature.

While the Au-related signal from the flat regions is due to the low-dimensional superstructure and reflects a chemical bond with atop Si atoms, the Au 4f core level emission from the islands identifies two distinct chemical environments: a metastable alloyed Au–Si mixture and a metal-like Au. On the basis of the already known features of the annealed Au/Si(111) interface [1], we ascribe the former component to the reacted skin covering the islands while the latter contribution is due to the Au-based island volume. A previous SAM investigation [7] established that this reacted skin is removed by soft ion-sputtering but can be restored by subsequent annealing. It should be noticed that the Gaussian FWHM of the Au 4f "reacted" component is larger by a factor of two than that used for Au metal. This reflects a variety of slightly inhomogeneous sites within the family of the "reacted" Au atoms which is consistent with non-stoichiometric compounds and points toward a metastable alloyed scenario.

We remark, however, that these laterally resolved measurements allow a significantly richer description of the Au/Si(111) interface when compared with the picture emerging from spatially resolved Auger line shape spectroscopy (SRALS) [7]. This is primarily due to the possibility of resolving via XPS line shape analysis a definitely much wider set of chemically distinct contributions local to the Au and Si sites. The SRALS measurements were based on an analysis of the broad Si $L_{2,3}VV$ Auger line shape, thereby allowing just a discrimination of the character of the majority of the Si sites at either the flat regions or the islands. However, no direct information concerning the Au sites was retrievable since the pertinent Au $M_{6,7}VV$ Auger line shape is inherently atomic-like in character thereby precluding an easy identification of the chemical environment local to the Au sites.

4. Conclusions

A laterally resolved photoemission investigation of thermally annealed Au/Si(111) interfaces has been reported. Spectra taken from selected points of the specimen surface, reflecting the distinct morphological pattern of the inhomogeneous interface (flat regions vs islands) yield a variety of chemically distinct environments local to the element-specific sites.

Acknowledgements

The authors are indebted to Marino Marsi, Sebastian Günther and Andreji Kolmakov for fruitful discussions. The critical reading of the manuscript by Alan Laine is greatly acknowledged.

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