Applied Surface Science 258 (2012) 3475–3484

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Comparative investigation of the $c(2 \times 2)$-Si/Cu(0 1 1) and $(\sqrt{3} \times \sqrt{3})R30^{\circ}$-$Cu_2Si$/Cu(1 1 1) surface alloys using DFT

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ARTICLE INFO

Article history:
Received 5 November 2011
Received in revised form
19 November 2011
Accepted 21 November 2011
Available online 29 November 2011

Keywords:
Surface alloy
Cu(0 1 1)
$c(2 \times 2)$
Copper silicide
PDOS
COOP
LCAO
DFT

ABSTRACT

The electronic structure of the $c(2 \times 2)$-Si/Cu(0 1 1) surface alloy has been investigated and compared to the structures seen in the three phases of the $(\sqrt{3} \times \sqrt{3})R30^{\circ}Cu_2Si$/Cu(1 1 1) system, using LCAO-DFT. The weighted surface energy increase between the alloyed Cu(0 1 1) and Cu(1 1 1) surfaces is 126.7 meV/Si atom. This increase in energy for the (0 1 1) system when compared to the (1 1 1) system is assigned to the transition from a hexagonal to a rectangular local bonding environment for the Si ion cores, with the hexagonal environment being energetically more favorable. The Si 3s state is shown to interact covalently with the Cu 4s and 4p states whereas the Si 3p state, and to a lesser extent the Si 3d state, forms a mixture of covalent and metallic bonds with the Cu states. The Cu 4s and 4p states are shown to be altered by approximately the same amount by both the removal of Cu ion cores and the inclusion of Si ion cores during the alloying of the Cu(0 1 1) surface. However, the Cu 3d states in the surface and second layers of the alloy are shown to be more significantly altered during the alloying process by the removal of Cu ion cores from the surface layer rather than by the addition of Si ion cores. This is compared to the behavior of the Cu 3d states in the surface and second layers of the each phase of the $(\sqrt{3} \times \sqrt{3})R30^{\circ}$-$Cu_2Si$/Cu(1 1 1) alloy and consequently the loss of Cu–Cu periodicity during alloying of the Cu(0 1 1) surface is conjectured as the driving force for changes to the Cu 3d states. The accompanying changes to the Cu 4s and 4p states in both the $c(2 \times 2)$-Si/Cu(0 1 1) and $(\sqrt{3} \times \sqrt{3})R30^{\circ}$-$Cu_2Si$/Cu(1 1 1) alloys are quantified and compared. The study concludes with a brief quantitative study of changes in the bond order of the Cu–Cu bonds during alloying of both Cu(0 1 1) and Cu(1 1 1) surfaces.

1. Introduction

Studies of metal (M) and transition metal (TM) silicides have burgeoned since the beginning of the 1980s due to their technological applications, particularly in both opto- and micro-electronics [1–7]. These studies have, in part, investigated the distribution of charge between the metal and the Si atoms and have demonstrated that one of the key requirements to understanding and controlling the properties of these systems is a clear elucidation of these charge distributions. The range of technical applications and the broad academic interest in these systems has necessitated both bulk and surface studies. Therefore, because of the relative novelty of detailed theoretical electronic surface studies of TM alloy, and particularly Cu–Si alloy, systems in this field, for example [8], both types of study were considered during the production of this work. The literature is extensive and particular reference is given in this work to articles that highlight dichotomies in the understanding of these systems. Recent studies [1] have identified that the role played by the metal atoms in nickel and molybdenum silicides is significantly poorly understood, to such an extent that crucial wavefunction characteristics such as the spatial distribution of the d band orbitals is barely, if at all, known. Earlier studies [3] which focused more on the bonding mechanism in silicides identified that the majority of valence charge was exchanged between the Si 3sp and TM 4sp bands, precluding a significant interaction with the TM 3d bands. In addition, studies [9] of 3d and 4d TM and M disilicide systems also highlighted the importance of the TM/M sp–Si interaction. However, photoemission studies [10] of 3d, 4d and 5d TM silicides have stated that Si s and p states and the TM d states are the key binding elements, and further X-ray emission studies [11] of 3d and 4d TM silicides have shown that in particular TM silicides the Si s and d states densities dominate. Much of the diversity in these works derives from the varying contribution of the metallic d states to the TM–Si or M–Si bond. By studying the interaction of Cu silicides the current work seeks to simplify these arguments by concentrating on a single TM with a complete d shell.

Many of the works in the literature review a range of TM/M's with significantly different valance. The current work simplifies this pedagogy by concentrating only on Cu silicides but bound differently, on the (0 1 1) and (1 1 1) faces of Cu. Also, the

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doi:10.1016/j.apsusc.2011.11.100

majority of surface studies have concentrated on metal deposition on semiconductor surfaces (see, for example [12]) and have relied on the minimization of surface stress [13] through the reduction of dangling bonds on the semiconductor surface as a mechanism to explain the extensive range of structures that form. The minority of studies has investigated silicide formation using the TM as the substrate. Fewer studies still have sought to elucidate the electronic structure of the silicide particularly on metal substrates [8, and refs. therein]. The current work is made possible by the clear structural elucidation of the *c*(2 × 2)-Si/Cu(0 1 1) surface alloy [14,15] which is shown in Fig. 1 together with the FCC, HCP and two-fold bridge phases of the $(\sqrt{3}\times\sqrt{3})R30^\circ$-$Cu_2Si$/Cu(1 1 1) alloy system. Comments about the electronic structures identified experimentally for the alloy [16] are included in the current work.

The current paper will therefore elucidate the electronic structure of the *c*(2 × 2)-Si/Cu(0 1 1) surface alloy and compare this structure with those for each phase of the $(\sqrt{3}\times\sqrt{3})R30^\circ$-$Cu_2Si$/Cu(1 1 1) alloy system. The work is organized as follows: in Section 2 an outline of the computational procedures used in the current work is presented, in Section 3 the main results and discussion are presented and the main conclusions of the work are included in Section 4.

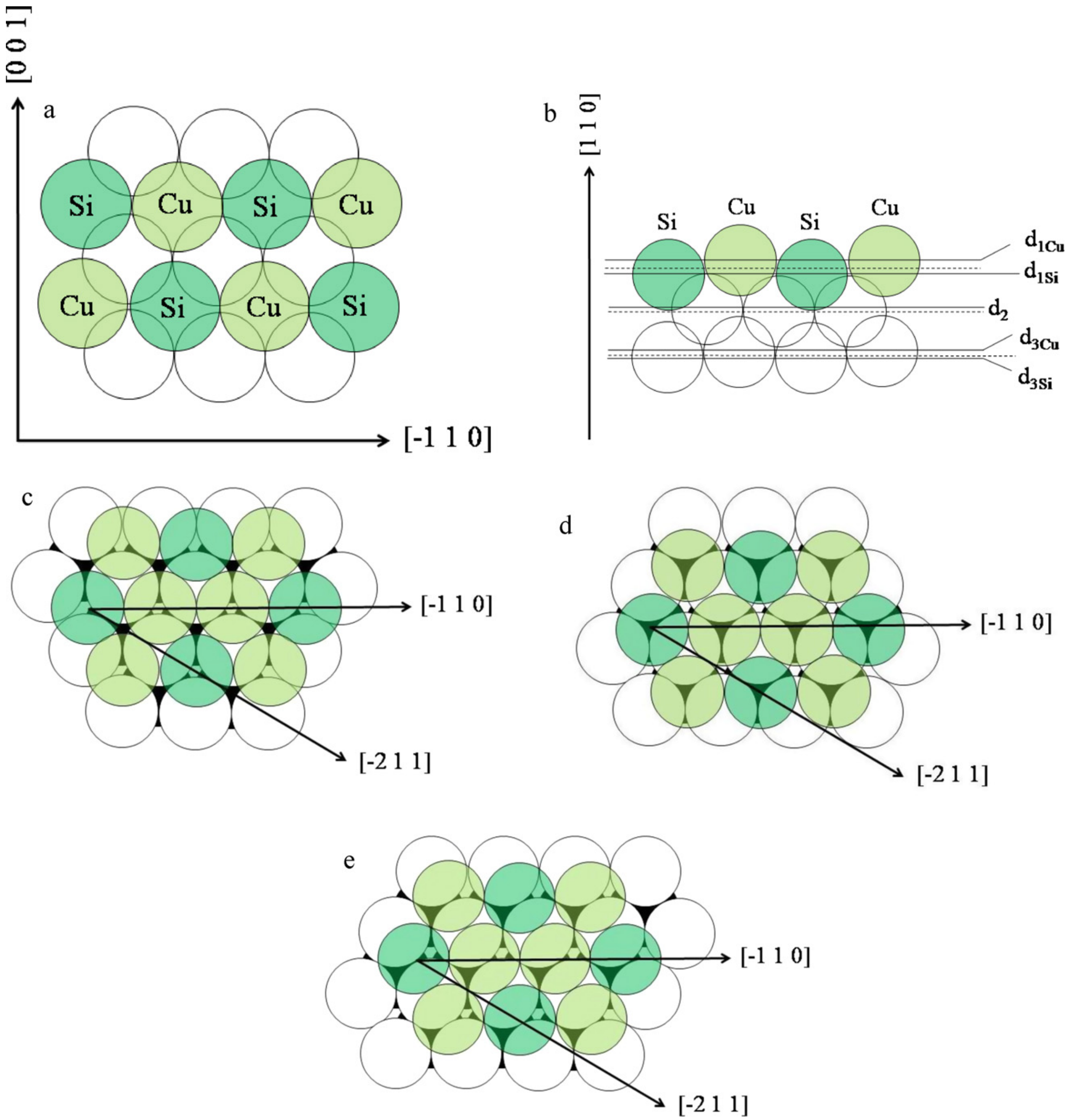

Fig. 1. (a) Planar, and (b) cross-sectional views of the *c*(2 × 2)-Si/Cu(0 1 1) surface, and the (c) FCC, (d) HCP and (e) two-fold bridge phases of the $(\sqrt{3}\times\sqrt{3})R30^\circ$-$Cu_2Si$/Cu(1 1 1) surface alloy. Parts (c), (d) and (e) of this figure are from [8]. The dark green circles represent surface Si ion cores, and the light green and clear circles represent surface and second layer Cu ion cores, respectively. In (a) the third layer of Cu ion cores lies directly underneath the surface layer ion cores. In (b) the labels d_{1Cu}, d_2 and d_{1Si} refer to the positions of Cu and Si ion cores, respectively. The labels d_{3Cu} and d_{3Si} refer to the positions of third layer Cu ion cores located directly beneath surface layer Cu and Si ion cores, respectively. The dashed lines in (b) represent the ideal bulk terminated positions of the ion cores.