Synthesis and characterization of copper nanostructures on silicon substrates

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Synthesis and Characterization of Copper Nanostructures on Silicon Substrates

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Abstract. Vacuum vapour deposition technique has been utilized for the synthesis of copper nanostructures on Si(111), Si(100) and Si(110) substrates at an optimized substrate temperature of 750°C. The samples are characterized by SEM, AFM and XPS. Their morphology is strongly governed by orientation of substrate. It is possible to realize the growth of triangular, square like and rod shaped geometries by choosing an appropriate orientation. This variation is attributed to the surface reconstruction which occurs at high temperature.

1. Introduction

Nanostructured materials are of great interest, because of their spectrum of applications in nanodevices and nanoelectronics. These nanostructures have unique physical, chemical and optical properties as their sizes stand intermediate between the bulk and atomic scales. As the bulk is reduced to the nano-scale, the electronic motions get confined i.e. fewer energy states are available for the electrons which results into a modified band gap in the nanomaterials. Besides, the nanomaterials also have increased surface to volume ratio. These properties of nanoparticles may be useful in biological, optoelectronics and gas sensing applications and semiconductors. In futuristic alternative metallization schemes for ultra large-scale integrated technology catering to the intensifying demand of the nanodevices in electronic applications, Cu is being considered as a potential replacement for Al. interconnects and its nanostructures thus have immediate relevance to the semiconductor technology [1]. In this respect the studies addressing to the synthesis of its dense arrays especially on Si and moreover interaction of Cu film with Si surface assume particular importance. Synthesis of copper nanoparticles has been extensively reported by various techniques which include chemical routes [2], electrochemical method [3], template assisted synthesis [4]. The yields achieved by these processes are less and they involve multiple steps. Also it is difficult to assemble them on Si substrates for their use in nano-devices.

In this paper we report the growth of nano islands of Copper on silicon substrates by vacuum vapor deposition technique and influence of orientation of Si suface on the morphology. It was observed that triangular, square like and rod shaped nanostructures with very precise morphology are formed on Si(111), Si(100), Si(110) respectively at an optimized substrate temperature of 750°C and the mechanism of formation of various structures has been discussed.

2. Experimental

Cu thin film were deposited on Si substrates of various orientations by simple vacuum vapor deposition technique in a vacuum system (Make:Hind High Vaccum Pvt Ltd model No.15 F6). Vacuum level of 5 x10^{-6} mbar was obtained by using Turbo Molecular Pump (TMP) backed by rotary pump. Prior to deposition the substrates were cleaned by ultrasonication in organic solvents. The substrates were mounted on a heater whose temperature was measured through a thermocouple and maintained using a temperature controller to accuracy of ± 5°C. The substrate temperature was varied between 550-850°C, and was maintained at for two hours prior to each deposition. The copper wire of 99.99 % purity was mounted in a Molybdenum boat for the evaporation. The film thickness was varied from 10-750Å using a quartz crystal thickness monitor, placed near to the substrate holder subtending normal angle to the incoming flux. The rate of deposition was maintained at 1Å/sec. After deposition the substrates were allowed to cool to room temperature before taking out of the chamber.

The samples were characterized by Scanning Electron Microscope (SEM) VEGA MV2300T/40 (TS 5130 MM TESCAN) to study the morphology and shape. Atomic Force Microscope (AFM) model JEOL JSPM 5200 with Rectangular cantilever of Si_3N_4 (length 200mm and width 40 mm) having force constant of 3N/m was also employed to study the morphology. EDX spectra was recorded to analyze the phase formation. X-ray Photoeletron Spectra were recorded using Al K source (CX-700) incorporated with MBE system EVA 32 R&D (Make: RIBER) and a MAC-2 electron energy analyzer. The binding energy scale was calibrated using Au $4f_{7/2}$ line of 83.9 eV. For XPS measurements the sample after deposition was immediately loaded to the high vacuum chamber to carry out analysis in order to minimize oxidation of the surface of the sample to verify if any oxidation phases are present in the sample.

3. Results and Discussion

At substrate temperatures of 550-650°C we observe a continuous film with spherical grains on all the substrates. As the substrate temperature is increased islands of definite shapes on different orientations of Si substrates are formed. Figure 1 shows a SEM image of 60 Å thick Cu film deposited at 750°C on Si(111). SEM image of similar film on Si(100) and Si(110) orientation are given in figure 2 and 3 respectively. It is observed that small islands of triangular, square and rod shaped patterns are distributed uniformly on Si(111), Si(100) and Si(110) substrates respectively. These structures are found to be dispersed uniformly all over the substrates and are oriented in a particular direction with respect to each other. The average size of these patterns is roughly equal with the edge length of the triangular island on Si(111) of the order of 300-400 nm. The sides of a square island on Si (100) is around 350 nm while the nanorods on Si(110) are of 50 nm diameter and the length is 2-3 μm. With increasing the thickness of the deposited Cu film the size of the nanostructures was found to remain almost constant in the range 10-100 Å. However in case of Si(100) substrate, with increase in thickness of the Cu film it was observed that few of the square like patterns getting elongated and form rod like structures. The EDX spectra confirmed the structures to be that of pure copper.

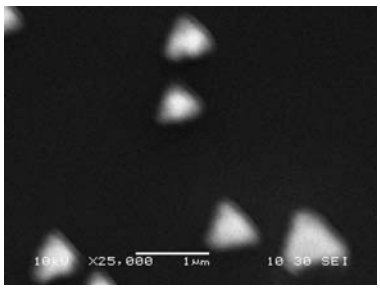

Figure 1. 60 Å Cu deposition on Si(111) at 750°C

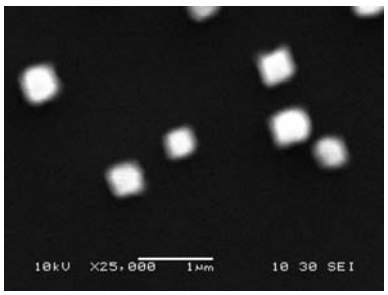

Figure 2. 60 Å Cu deposition on Si(100) at 750°C

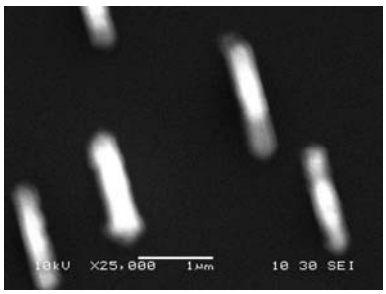

Figure 3. 60 Å Cu deposition on Si(110) at 750°C

The AFM of 10 Å Cu deposited on Si(111), Si(100) and Si(110) is shown in figure 4, figure 5 and figure 6 respectively. It is observed that with increase in height the dimensions of the structures decreases which gives it a tapering shape. The height of these nanostructures for a 10 Å thick film on all the substrates was found to be of the range of 200 nm. With increase in film thickness the height of the nano structures was found to increase. The height for a film thickness of 100 Å was observed to be around 450 nm. AFM images also show layer like structures. Thus we observe the formation of self assembled nano structures of copper on Si substrates when the substrate temperature is around 700°C.

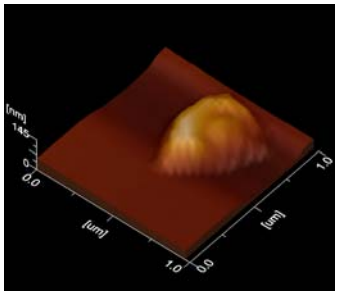

Figure 4. 10 Å Cu deposition on Si(111) at 750°C

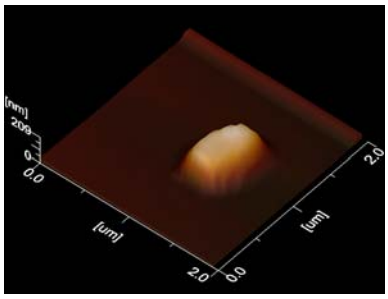

Figure 5. 10 Å Cu deposition on Si(100) at 750°C

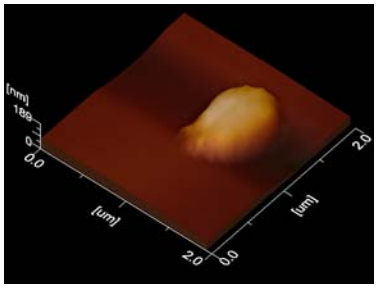

Figure 6. 10 Å Cu deposition on Si(110) at 750°C

X-ray photoelectron spectroscopy (XPS) was carried out on 100Å thick Cu film deposited on Si(111) substrate at 750°C. XPS is a surface sensitive analytical tool which indicated the phase present on the surface. Figure 7 shows XPS spectra of Cu 2*p* peak. The two peaks corresponding to Cu $2p_{1/2}$ and Cu $2p_{3/2}$ is observed. However, the absence of any satellite peak between the two peaks indicates that there is no oxide formation on the surface. The Auger parameter was also calculated for the copper peak which indicated that the formed nanostructures are that of metallic copper. The O 1*S* spectra is shown in figure 8. This peak can be deconvulated into two peaks one which corresponds to adsorbed oxygen and the other which arises from the presence of SiO_2 on the surface of the substrate. Thus it is confirmed that the observed nanostructures are of pure copper.

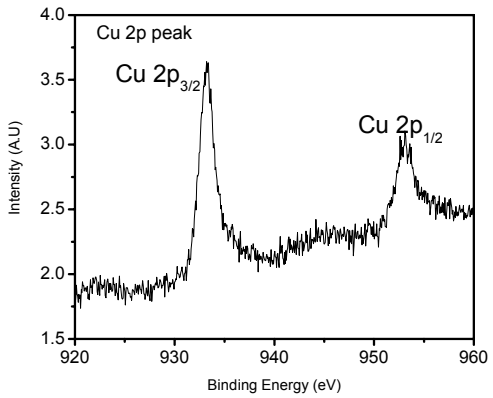

Figure 7. XPS spectra of Cu nanostructure deposited on Si(111) substrate for Cu 2*p* peak

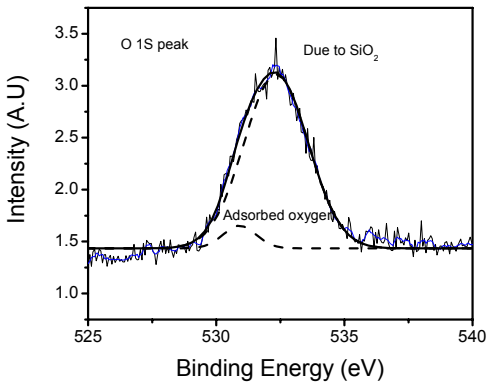

Figure 8. XPS spectra of Cu nanostructure deposited on Si(111) substrate for oxygen 1*s* peak

We have observed the formation of self assembled nano structures of copper on silicon substrates. It is clearly seen that the orientation of the substrate was found to play an important role on the shape of

the nanostructure. Similar kind of reports are there in the literature where very thin layer (few monolayers) of metal film has been deposited on atomically clean and reconstructed Si substrates. Sekar et al [5] has reported the formation of triangular gold/gold silicide islands on Si(111) substrate. Growth of Pt silicide nanowires on Si(100) substrate has been reported by Lim et al [6]. Parajuli et al has also reported the formation of copper silicide nanobeams on Si(100) substrates [7].However the mechanism behind the shapes has not been extensively investigated.

It is found that the pattern formation on the silicon substrates is attributed to the silicon reconstruction taking place at very high substrate temperature [8]. The reconstruction takes place at solid vacuum interface in order to minimize the dangling bond to attain minimum energy configuration. When a Si substrate is heated to high temperature in vacuum the dangling bonds rearrange the, self to minimize the surface energy. When adatoms approach these substrates they get attracted to these sites of minimum energy and take their shape.

In case of Si(111) substrate the most commonly reported surface reconstruction is the Si(111)-(7 x 7) [9, 10]. The driving force for the formation of the (7x7) reconstruction is the reduction of the number of dangling bonds by the formation of *dimers*, *adatoms* and a *stacking fault*. The unit cell of (7x7) reconstruction of the Si(111) surface is of rhombic shape which consists of two different triangular half unit cells (HUC), one with a *stacking fault* (faulted half) and one without a *stacking fault* (unfaulted half) with respect to the bulk. This reconstruction leads to a reduction of the surface energy. The nucleation of adatoms on this surface takes place at these triangular half unit cells and thus we obtain triangular nanostructures on reconstructed Si(111) susbtrate.

The most generally reported reconstructions of the Si(100) surface is the Si(100)-(2x1) [8]. The 2x1 reconstruction is supposed to be its lowest energy ground state configuration. Prior to the reconstruction, each Si atom on the surface has two dangling bonds. During the reconstruction the Si atoms of the surface layer forms a covalent bond with an adjacent surface atom and thus are drawn together to form a dimer. These dimers arrange themselves in a row perpendicular to the dimer axis. In the initial stages of growth the adatoms nucleate on the dangling bonds of the dimer row and form a square like nano-structure. Since the mobility of atoms is high along the dimer rows and low across them, with increase in number of adatoms on the Si(100)-(2x1) surface, the atoms arriving on the sides of the square islands are transported to ends along one direction, resulting in 1-D growth. Thus the square islands gets elongated resulting in to the growth of Cu nanowire like growth on the Si(100) surface at few places at higher thickness [7]. The length of these wires are found to be along two perpendicular directions because of the stacking sequence in the Si(100) substrate, the dimers are rotated by 90º on two adjacent terraces separated by a monoatomic step.

Si(110) surface exhibits a 16x2 reconstruction [11]. The adatom-tetramer-interstitial (ATI) reconstruction in this case yields the lowest surface energy for models of the Si(110) 16 x 2 surface with terraces [12]. Similar to the above two cases, the arriving adatoms nucleate on these trenches and grow along the direction of the unit cell of the reconstructed surface. This gives rise to the growth of nanorods with their long axis parallel to each other.

Thus the surface reconstruction happening on the Si substrate surface at 750°C explains the formation of these self assembled nanostructures of Copper. Thus we have been able to achieve nanopatterns of Cu on Si substrate by a simple technique which can have technological application in various nanodevices.

4.Conclusion:

We have fabricated self assembled array of copper nanostructures on silicon substrates of different orientations. The islands formed are distributed uniformly on the substrate and are aligned in a specific direction. The substrate temperature is found to play a key role in the island formation as pattern formation is found to occur only at temperature around 750°C. The reconstruction of Si surfaces at higher temperature was found to be responsible for the shape of of these nanostructures.

5.Acknowledgement
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