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Epitaxial growth of µm-sized Cu pyramids on silicon

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Abstract Triangular and quadratic Cu pyramids were epitaxially grown on Si(111) and Si(100) substrates, respectively, by pulsed laser deposition at elevated substrate temperatures above 200°C as well as by post-annealing of closed Cu layers prepared at room temperature. In both cases, three-dimensional pyramids with edge lengths of up to 9 µm were obtained, as observed by scanning electron microscopy and atomic force microscopy. Although the macroscopic shape is a pyramid, microscopically the islands consist of columnar grains (with lateral sizes of only about 50 nm at 260°C). The size and shape of the pyramids can be controlled by the substrate used, the amount of material deposited, and the temperature during deposition or annealing. Additionally, first hints were found that the pyramids can be aligned by structuring the substrate. The formation of such large pyramids is explained by a fast diffusion of Cu atoms on Si over distances of some µm and a high jump probability to higher pyramid layers.

1 Introduction

Single metal films deposited on surfaces are of large technical interest for instance as protecting layers, mirrors, or conducting lines. The grain sizes, grain orientations, and grain boundaries within the films strongly influence their properties. In recent years, Cu has replaced Al as the interconnect metal of choice in microchip fabrication due to a higher conductivity and a higher resistance to electromigration and stress migration, and due to the low production costs. But, the main drawback of Cu is its high diffusivity leading to the formation of interface reactions such as Cu silicides in the case of Si substrates [1–3]. Also, a formation of Cu islands with pyramidal shape was observed after annealing of evaporated Cu films on Si substrates at higher temperatures or reaction of Si with gaseous cuprous chloride [3, 4]. The formation of Cu pyramids also occurs on Cu substrates during evaporation and on Au during electrodeposition [5, 6]. Such a three-dimensional growth mode during thin-film deposition was first predicted by Villain and later seen in computer simulations by Siegert and Plischke [7–9]. Furthermore, periodic ordering of such nanostructures on crystalline substrates is a topic of actual interest. Especially on faceted substrates spontaneous ordering exists and is a convenient technique to get ordered arrays of quantum dots (see e.g. [10]).

The aim of this paper is to systematically study the formation of Cu pyramids on Si substrates during pulsed laser deposition (PLD). We will show that epitaxially grown µm-sized pyramids can be formed at higher substrate temperatures as well as during post-annealing of Cu layers. The size and shape of the pyramids can be tuned by the substrate or annealing temperature, material quantity, and substrate orientation. We will further show that microscopically the pyramids consist of columnar grains with lateral sizes of only about 50 nm. Additionally, results on a periodic arrangement of the Cu pyramids and a possibility to protect them against decay are described.

2 Experimental setup

All Cu films were pulsed laser deposited on Si(111) and Si(100) substrates using a standard PLD setup in an ultra-high-vacuum (UHV) chamber with a base pressure of

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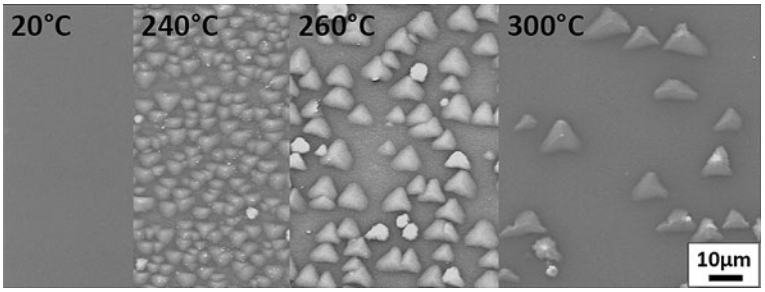

Fig. 1 SEM images of Cu films deposited on Si(111) at different substrate temperatures showing the formation of pyramids above 200°C

10^{-8} mbar [11]. A KrF excimer laser with wavelength of 248 nm, pulse duration of 30 ns, and repetition rate of 10 Hz was used. A laser fluence of 6.5 J/cm^2, a target-to-substrate distance of 50 mm, and substrate temperatures between room temperature and 300°C were taken. The deposition rate of Cu was determined by profilometry to be about 0.004 nm/pulse.

The morphology of the films was analyzed using scanning electron microscopy (SEM, Cambridge Instruments S360). The heights of the Cu pyramids and angles with the substrate were determined by atomic force microscopy (AFM, NanoScope 4, Veeco). The epitaxial relation between substrate and Cu film was examined via X-ray diffraction (XRD) experiments (Siemens D500, Co-K_α radiation). Four-point resistance measurements were done during heating with a rate of 1 K/min. To analyze the inner structure of the Cu islands, TEM lamella were prepared by a focused ion beam (FIB) system (Nova Nanolab 600) and studied in cross section by transmission electron microscopy (TEM, Philips CM30).

3 Results and discussion

First, 40-nm-thick Cu films (corresponding to 10 000 laser pulses) were grown on Si(111) and Si(100) substrates at room temperature. In the SEM, the film surfaces appear smooth and do not show any contrast except for the occurrence of some droplets as typically expelled from the target during PLD (see Fig. 1, on the left) [11, 12]. X-ray diffraction patterns reveal that the films exhibit a preferred (111) orientation on Si(111) and a (200) orientation on Si(100), respectively (Fig. 2). This indicates that the orientation of the substrate strongly influences the orientation of the Cu grains. While the (111) orientation on Si(111) is typical for a fcc structure due to the close packing of the (111) plane (and is also observed on an amorphous glass substrate), in the case of Cu on Si(100) the strong (200) reflection is a first sign for epitaxial growth.

In the next set of experiments, Cu films were grown on both types of substrates at different high substrate temperatures using a fixed number of 10 000 laser pulses. Up to about 200°C, the film surfaces are smooth in SEM micrographs on both substrates (except for the droplets). But, above this temperature, on Si(111) a high number of µm-size Cu islands with triangular pyramidal shape become resolvable in the SEM (Fig. 1). The pyramids are parallel arranged, clearly indicating an epitaxial growth of the Cu pyramids. Additionally, they are well separated on a µm scale. Obviously, the surface diffusion of Cu on Si is very fast at these temperatures. Also, on Si(100), epitaxially grown Cu pyramids become visible above 200°C (Fig. 3). But, now, the pyramids have a (more or less) quadratic shape due to the different symmetry of the substrate. Interestingly, the edges of some of the quadratic pyramids are frazzled, indicating that the growth of these pyramids is not perfect.

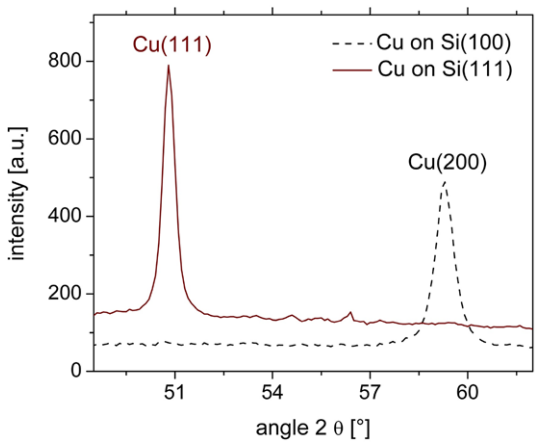

Fig. 2 X-ray diffraction patterns of 40-nm-thick Cu films deposited on Si(111) and Si(100), respectively, at room temperature (Co-K_α radiation)

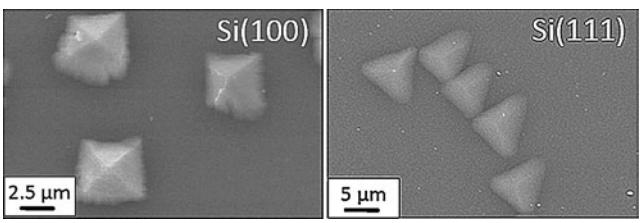

Fig. 3 SEM images of Cu films deposited on Si(100) and Si(111), respectively, showing the different shapes of the pyramids depending on the substrate orientation. One should note that the edges are frazzled

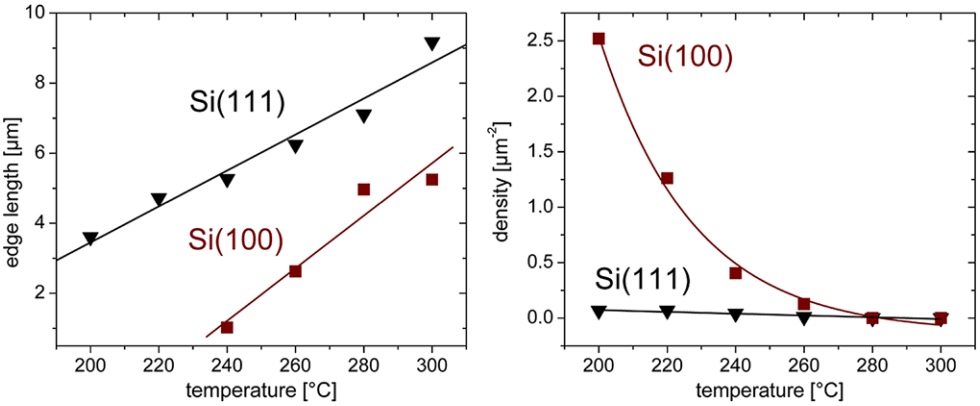

Fig. 4 Temperature dependence of the edge lengths and densities of the Cu pyramids formed on Si(111) and Si(100), respectively

The occurrence of these frazzled structures is a hint for a relatively low edge diffusion of Cu, not being able to straighten the edges of the pyramids. On both different substrates, with rising substrate temperatures the islands increase in size, while simultaneously their density is lowered. This enlargement is expected for a nucleation and growth process of islands with increasing temperatures, because the surface mobility of the Cu atoms on Si increases with temperature and thus the probability of hitting an already formed Cu island enlarges for an atom diffusing on the substrate surface. It should be noted that the Cu pyramids grown on Si(111) at 300°C have lost their nearly perfect triangular base shape, visible in an elongation of the corners and curved edges, respectively. Obviously, at this temperature the edge diffusion of Cu is not sufficient to straighten the edges of the triangular basal plane of the pyramid and instead of staying at the edges many of the atoms jump to higher planes forming the pyramid. In summary, at the chosen fixed pulse number of 10 000, 'best formed' triangular-shaped pyramids are obtained at 260°C.

The edge lengths of the two types of pyramids as well as the island densities are depicted in Fig. 4, for comparison. It can clearly be seen that the triangular pyramids on Si(111) are larger than the quadratic pyramids on Si(100) at all temperatures. Simultaneously, a higher island density is obtained on Si(100). From both results, one can conclude that the surface diffusion of Cu depends on the substrate orientation and is much larger on Si(111) than on Si(100).

Now, the shape and geometry of the two types of pyramids were analyzed in more detail. Performing SEM measurements on samples tilted in the SEM, it can be recognized that the height of the pyramids on Si(111) is always typically 10 times smaller than the edge length (Fig. 5). Furthermore, some of the pyramids have bent edges or planes, showing that the formation of these pyramid structures is kinetically (and not thermodynamically) controlled by a low edge diffusion of Cu and a high jump rate to higher atomic planes.

Some of the more perfect pyramids were analyzed by AFM to study the shape, edge directions, and plane orientations in more detail (see Fig. 6). For triangular pyramids on Si(111), the angles between side planes and substrate surface are very small (in the range of 5–8°), indicating again that the pyramids are relatively flat. This means that the surface planes of the pyramids obey high Miller indices, as already observed by Yasue et al. [13]. In comparison, on Si(100) the quadratic pyramids have a smaller base, but a larger height. Thus, the corresponding angles of the quadratic pyramids are a little larger (in the range of 10°–14°). These differences can be explained by a lower edge diffusion of Cu at the base of the quadratic pyramids, but a higher jump probability towards higher planes and a faster diffusion of Cu on Cu. An interesting detail can be observed on many of these pyramids, namely that they exhibit a hip roof as marked in Fig. 6 by lines.

Exemplarily, for a quadratic pyramid with an edge length of 5 µm, a height of 800 nm, and an angle of 17.7° between the side surface and the substrate surface, the percentage of atoms in the basal plane and the (net) jump probability to higher planes were calculated by simple geometrical arguments. It was found that only 0.005% of the about 3×10^{11} atoms of the whole pyramid are located in the under-most Cu layer and thus 99.995% of the atoms jump from the basal plane to higher atomic layers of the pyramid, when hitting

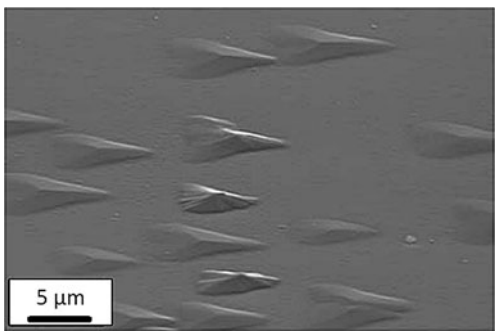

Fig. 5 SEM image of a Cu film on Si(111) after tilting the sample in the SEM by 60°, clearly showing that the heights of the pyramids are much smaller than the edge lengths

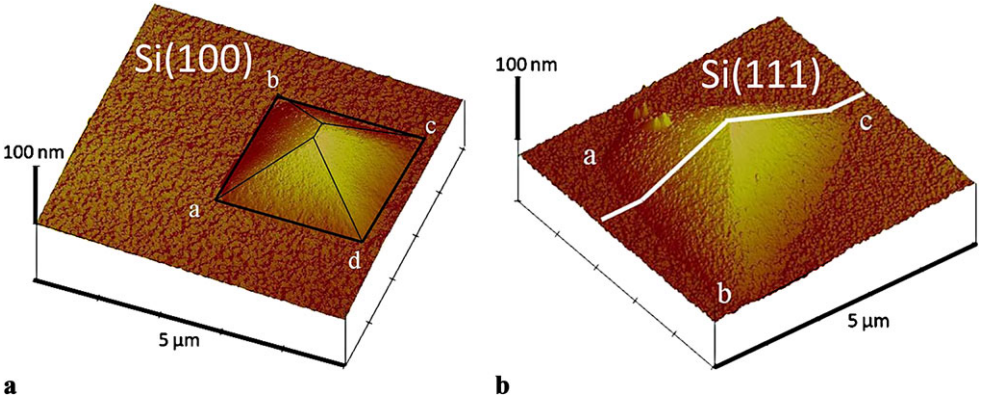

Fig. 6 AFM images of Cu pyramids **a** on Si(100) and **b** on Si(111)

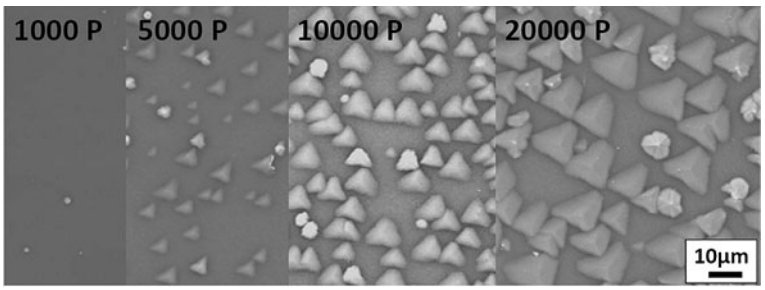

Fig. 7 SEM images of Cu films showing the increase of the pyramid size with the number of laser pulses *P*

the pyramid after adsorption and diffusion on the Si substrate.

The size and density of the pyramids obtained at a given substrate temperature can be tuned by the amount of Cu deposited on the substrate surface (see Fig. 7). For this, the number of laser pulses was varied from 1000 to 20 000 pulses. As substrate temperature, 260°C was taken, because at this temperature the 'best triangular-shaped' pyramids were observed on Si(111). As expected, the average size of the triangular pyramids continuously increases with the number of laser pulses but, at low pulse numbers, the islands are still too small to be resolved at a magnification of 10 000 in the SEM. Additionally, coalescence processes take place as soon as islands hit each other. The average height of the pyramids first increases with the number of laser pulses, until it reaches a constant height of about 400 nm, although the pyramids further increase in size. Obviously, a critical pyramid size is achieved at 10 000 pulses; above that, the Cu atoms hitting the base of the pyramid cannot diffuse far enough on Cu to reach the top of the pyramid. Thus, the diffusion of Cu on Cu is the limiting mechanism and the average height of the pyramids also stays constant when depositing more material on the substrate.

Furthermore, TEM experiments were performed in cross section to look at the inner microstructure of the pyramids in more detail. For this, the pyramids were first covered by a thin Pt layer and then a slice from the pyramid was cut by FIB. From the external shape of the pyramids one could assume that they are single- or microcrystalline. This is not the case at all, as can be seen in Fig. 8. The pyramids consist of lots of columnar grains with a diameter of only about 50 nm and a length which is equal to the local height of the pyramids. Below the pyramid, the Si substrate is curved, indicating that the Cu pyramids produce stress on the subjacent Si substrate. The columns possess different lateral orientations, as can be seen by the different contrasts of the columns, which is surprising, because the macroscopic shape and alignment of the pyramids are clearly an indication for epitaxy. Whether the different orientations of the columns are induced by lattice mismatch between Cu and Si, or are twinned grains reducing the film stress during growth,

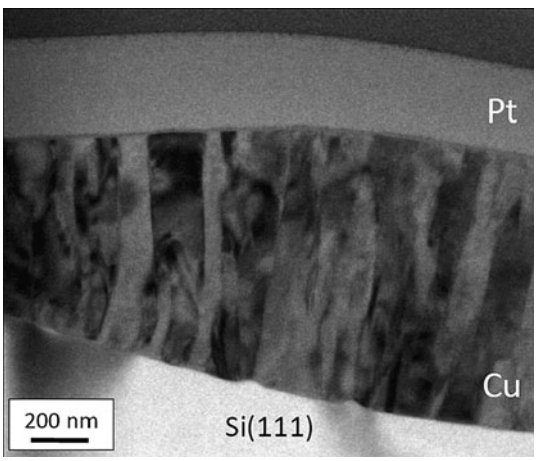

Fig. 8 Cross-sectional TEM image of a part of a Cu pyramid (covered by Pt) on Si(111)

is still under investigation. But, the occurrence of the columnar grains with different orientations can probably explain that the edges of some pyramids are frazzled, as shown in Fig. 3. Anyway, indications for a Cu_3Si or other Cu-silicide interlayer (such as for instance observed by Jiang et al. [14]) transferring the epitaxy between Cu and Si, were not found in the cross-sectional TEM investigations.

In a further set of experiments, it was studied whether the two types of pyramids can also be formed by post-annealing of continuous 40-nm-thick Cu films grown at room temperature. Indeed, above about 200°C, the films transform on both substrates into the same types of pyramids as observed above. But, large differences exist, when comparing the sizes and densities of the two kinds of different heated films in more detail. After post-annealing, the pyramids are much smaller, have a higher island density, and the sizes of the pyramids are almost temperature independent after annealing to temperatures of 220–300°C. In the case of the triangular and quadratic pyramids, average edge lengths of only about 2.5 µm and 1 µm, respectively, were observed. The occurrence of larger pyramids in the case of a deposition at elevated substrate temperatures can be explained by a high surface diffusion of Cu on Si, while the volume diffusion, necessary for the transformation of the closed Cu layer into islands, is much lower, leading to higher nucleation rates and thus to smaller pyramids.

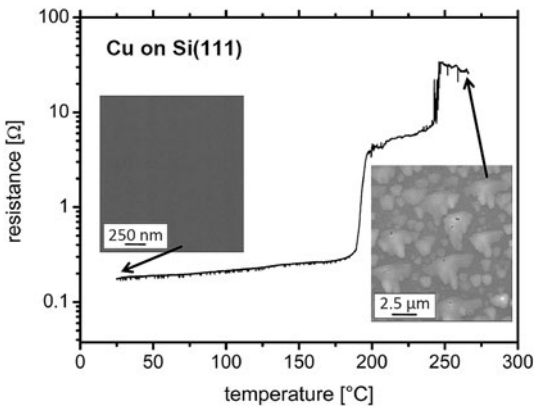

Fig. 9 Change of the resistance of Cu on Si(111) during annealing. In the inset, SEM images are depicted showing the surface structure of the Cu film at room temperature and after annealing up to 270°C

The transformation of continuous Cu films into pyramids was further studied by in situ resistance measurements, performed parallel to the film surface during annealing up to 270°C. The transformations take place in two steps (see Fig. 9). Up to about 180°C, only a slight change of the resistance is observed. This is the temperature range where the film is still smooth and no pyramids are visible in the SEM. Then, a step-like resistance increase occurs at about 200°C as soon as the film starts to transforms into pyramids. In the temperature range between 200 and 240°C, the resistance only slightly increases and the size of the pyramids remains almost constant. From the fact that a relatively low resistance is measured, it can be concluded that the pyramids are interconnected at their basal planes by a remaining Cu layer. Then, a second step-like resistance increase occurs at 240°C. Probably, further parts of the continuous film are transformed into pyramids. Why this transformation proceeds in two well-defined steps and not continuously is not understood so far.

Furthermore, different influences on the growth and stability of the Cu pyramids on Si were investigated. First, it was found that the formation of Cu pyramids is prevented as soon as the Si substrates exhibit a SiO_2 layer with a thickness of more than 3 nm. Then, the epitaxial growth is hindered and only spherical Cu islands are formed. From earlier experiments, we know that during the first laser pulses thin SiO_2 layers are resputtered due to the high amount of energetic ions (up to 50% with energies of about 100 eV) hitting the substrate during PLD [15]. Then, Cu is directly deposited onto the 'laser-precleaned' Si surface. Additionally, all kinds of impurities on the Si surface act as nucleation sites and lead to smaller pyramids or even a loss of the pyramidal shape of the islands (see Fig. 10a). Also, the ambient atmosphere leads to dramatic changes of the pyramids after deposition, when keeping them in air (Fig. 10b). On a time scale of days a degradation of the pyramids takes place, ending in a partial corrosion after months. The reason for this could be the relatively open structure of the pyramids seen in the frazzled edges and the columnar microstructure. Therefore, hydrogen or other components (for instance acids) can diffuse into and penetrate along the grain boundaries taking off poorly bound atoms. Nevertheless, it was found that the pyramids remain stable in air when they are covered by a 20-nm-thick Cr layer before leaving the UHV chamber.

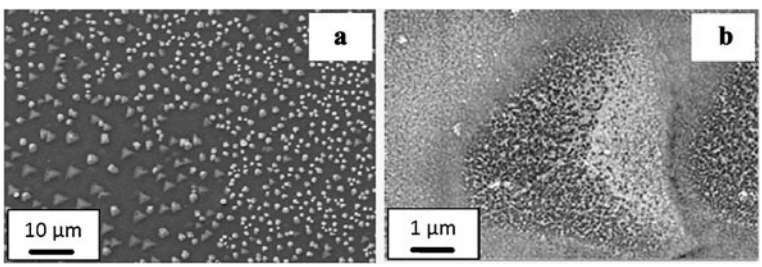

Fig. 10 SEM images of Cu films with pyramids on Si(111). In **a** one can see that impurities (*on the right of the image*) lead to a loss of the pyramidal structures and conventional island growth instead. In **b** the influence of an ambient atmosphere on a Cu pyramid is depicted

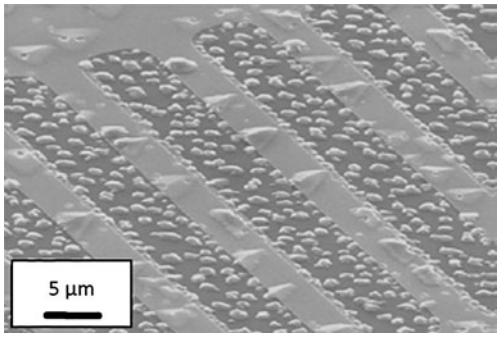

Fig. 11 SEM image of Cu on a structured Si(111) substrate. *On the remaining lines* the *triangular pyramids* are more or less periodically aligned. In between, the surface is roughened and thus the islands have a round shape

Finally, it was observed that the pyramids are often aligned along defects existing on the substrate, such as for instance scratches. It is obvious that such defects act as nucleation centers increasing the number of pyramids with lowered size along scratch lines. Also, first experiments were done to prove whether the pyramids can be aligned by structuring the substrate with electron-beam lithography. In Fig. 11 the deposition of Cu on a structured Si surface is depicted, where about 5-µm-broad lines were produced. On these lines the triangular pyramids are indeed more or less periodically aligned, while in the space in between the lines, where the Si surface was roughened due to ion milling, the pyramidal shape of the islands is lost.

4 Conclusions

In summary, it was shown that well-separated triangular and quadratic Cu pyramids can be epitaxially grown on Si(111) and Si(100) substrates, respectively, by pulsed laser deposition at elevated substrate temperatures as well as by post-annealing of closed Cu layers prepared at room temperature. In both cases, pyramids with µm size are obtained at substrate or post-annealing temperatures above 200°C due to a high diffusion of Cu on Si. But, in comparison, the diffusion of Cu atoms on Si(100) is lower than on Si(111), as can be seen in the higher number and smaller size of the quadratic pyramids compared to the triangular pyramids. The size and shape of the pyramids can be controlled by the substrate used, the amount of material deposited, and the temperature during deposition or annealing. The shape strongly depends on a complex interplay of the mobility of Cu atoms on Si and along the bottom pyramid edges, their jump probability to higher pyramid planes, and their mobility on the Cu pyramid layers.

Cu-silicide interlayers transferring the epitaxy between Si and Cu did not show up in the cross-sectional TEM measurements. Whether energetic particles occurring in PLD are responsible for the growth of the Cu pyramids directly on Si is not clear. Probably, the size and shape of the pyramids can be influenced by a reduced kinetic energy of the deposited particles in an inert gas pressure during PLD [15]. Further studies to understand the inner microstructure of the pyramids, the structural changes with alloying, and the transformation processes observed during post-annealing, are on the way.

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