Pinhole formation in solid phase epitaxial film of CoSi$_2$ on Si(111)

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The long-standing pinhole problem in solid phase epitaxial growth of a CoSi$_2$ film on Si(111) has been revisited with *in situ* scanning tunneling microscopy. While the as-deposited film with 5 Å of Co at room temperature shows a smooth granular texture with original substrate terraces remaining intact, annealing at 580 °C produces an epitaxial CoSi$_2$ film with large pinholes enclosed by a thin ring CoSi$_2$, exhibiting a volcano feature. Quantitative analysis shows that the formation of pinholes is a result of rapid Si outward diffusion from bulk to surface, and of the subsequent Si reaction with Co on the outer surface. Evidence suggests that inhibiting the Si diffusion channels during the thermal annealing process is the key to solving the pinhole problem. © 1998 American Institute of Physics [S0003-6951(98)03926-6]

Owing to its low resistivity and good epitaxial alignment with a Si substrate, CoSi$_2$ has emerged as a leading choice of the contacting material in future generation Si devices. So far, however, CoSi$_2$ has failed to find wide application due to the lack of integrable fabrication procedures necessary to achieve a high quality film. One of the major difficulties is the unavoidable presence of sizable pinholes in CoSi$_2$ films, produced by molecular beam epitaxy (MBE) or by solid phase epitaxy (SPE), which can lead to an undesirable large current leakage and ultimately to the device failure. This problem is even more fatal as the dimension of devices continues to shrink. Considerable efforts have been devoted to solve the pinhole problem by various deposition and reaction schemes but only limited success has been achieved in laboratories. Although smooth silicide film could be obtained via a precise control of co-deposition of Co and Si at room temperature (RT) or at 400 °C, large pinholes inevitably appear following a subsequent annealing near 600 °C, which is a mandatory step to improve the electrical conductivity. Pinhole-free CoSi$_2$ film has reportedly been obtained in mesoaxy using high energy and high dose ion implantation, but this method requires dedicated tools which are not practical in conventional Si processing. More recently, a number of template mediated growth methods, such as using Ti or oxide as an interlayer, have shown promising results for a pinhole-free CoSi$_2$ fabrication procedure.

Despite being a long-standing problem, the true origin of the pinhole formation in CoSi$_2$ has not yet been satisfactorily established. Surface and interface energies are the most common source of reasoning by many authors since the formation of pinholes could be the easiest kinetic pathway to reach a reduction of surface and interface energies. Experimental findings are, however, much less in unison. Early on, this problem was described as a dewetting process driven by either a smaller surface energy for the Si(111) than for CoSi$_2$ or by a high interface energy. But this simple model is inconsistent, respectively, with the fact that Si islands tend to form on CoSi$_2$ (Ref. 3) and that CoSi$_2$ layers with a Si rich surface exhibit good thermal stability. The relief of the misfit stress in the CoSi$_2$ layers had also been sought as the reason behind the pinhole formation. Measurements of the lattice parameters with and without a high density of pinholes, however, showed that pinholes have no effect on the film strain. SPE-grown CoSi$_2$ often contains a fraction of type-A orientation as intermediate phases. The idea that the conversion of type-A into type-B grains could be related to the pinhole formation was thus proposed, but only to be abandoned shortly after since even in SPE-grown single crystal CoSi$_2$, pinholes were found to be unavoidable. By carefully controlling the deposition, the surface of CoSi$_2$ can be made to have a CoSi$_2$-C (Co rich) or a CoSi$_2$-S (Si rich) structure, with the latter being a more stable one against thermal annealing. It was found that the transformation from the former to the latter is accompanied by the pinhole formation. Therefore the energetic difference between these two phases was identified as the responsible factor for the pinhole problem. This latest idea has also been challenged by a scanning tunneling microscopy (STM) study showing pinholes occur even on an initially Si-rich film upon annealing. Furthermore, it may also be questioned why the segregation of Si must be achieved through delivery from pinholes rather than bulk diffusion in view of a recent experiment which has shown that Co diffusion in bulk Si far surpasses that on its surface. In short, conflicting findings seem to exist for every mechanism proposed so far. It is clear that energetic consideration alone cannot account for the diverse experimental data, and a more adequate model must also include the detailed role of the kinetics involved.

In an attempt to obtain the microscopic origin of the pinhole formation, we have carried out an *in situ* study of SPE growth of CoSi$_2$ on Si(111), using STM to reveal the surface morphology associated with the deposition and silicidation procedures. In this letter we present direct evidence showing that the pinhole formation is a consequence of Si outward diffusion from bulk to surface and the subsequent Si reaction with Co on the outer surface to form a ring of CoSi$_2$ around the pinhole. This observation suggests that attention should be shifted towards the understanding of the origin and introduction of the diffusion channels during thermal processing. Inhibiting these channels could hold the key to a successful prevention of the pinhole problem.

The experiments were carried out in an ultrahigh...
running along the original orientation of the bare substrate with the same straightness. Higher resolution scans such as those shown in Fig. 1(b) reveal that the terraces have a uniform and smooth granular texture. The averaged grain is 2.5 Å high and 25 Å wide. Auger measurements show that our sample contains a Co rich mixture with about 30% content of Si near the surface as a result of the RT reaction. These results are consistent with earlier reports on RT Co deposition.

Annealing the as-deposited sample at 580 °C yields an epitaxial CoSi2 film which gives rises to a sharp (1 × 1) LEED pattern. Figure 2 shows the typical STM images of the annealed sample. Two important features are quite visible in these images. First, a larger number of randomly distributed deep voids (dark patches) appear in the sample [Fig. 2(a)]. These are the well-known pinholes. The opening of the pinholes ranges from 500 to 1500 Å and the depth varies from 20 to 50 Å, surpassing the CoSi2 /Si interface roughly 20 Å below the surface in agreement with the earlier STM study. 7 Second, apart from these pinholes, the granular texture in the as-deposited sample is now replaced with atomically flat terraces. The 5 Å Co deposition should yield ~20 Å of CoSi2. It is quite remarkable that there is no significant increase in the step meandering or change in the step density after annealing. A step morphology resembling that of the substrate original substrate step morphology in the CoSi2 film was attributed to limited lateral diffusion at RT. 18

Quite notably, higher resolution STM images, such as seen in Fig. 2(b), further reveal that many of the pinholes are each fully or partially enclosed by an elevated bank of CoSi2, 3–11 Å high and 500–1000 Å wide. The distinct volcano feature of the pinhole indicates a strong correlation between the Si atoms that are removed from the pinhole and its surrounding CoSi2 islands. To understand the underlying relationship, we compare the volume of pinholes, Vhole, with that of its surrounding islands, Vinland. We measure the height of the islands and the depth of the pinhole with respect to the nearby flat terraces and approximate the pinhole with straight walls. To minimize the errors, we only use pinholes with an opening sufficiently large to allow the tip to reach its bottom. Figure 3 plots Vinland against Vhole, for 18 isolated holes in two different samples, and the straight line is a least square fit to the data. It shows that within the accuracy of our measurement, Vinland/Vhole is essentially a constant and equal to 0.9. It follows from the atomic densities of the reactants that, for a given quantity of Si, the relative volume between CoSi2 and Si is VCoSi2/VSi = 0.84, i.e., to grow 32 Å of CoSi2 one needs to consume 10 Å of Co and

FIG. 1. (a) A 1.5 μm×1.5 μm STM image of 5 Å Co deposited on Si(111) at RT. (b) A higher resolution scan (770 Å×5000 Å) showing a granular texture of the surface with a vertical corrugation of ~2.5 Å. The lateral grain size varies from 20 to 30 Å.
obtain a precise dimension and shape of the pinholes.

Based on our STM results and the above quantitative analysis, we postulate that during the postdeposition annealing some diffusion channels are activated to expose the Si substrate, permitting a significant mass transport from bulk Si to the surface. The arriving Si atoms react with Co atoms from the outer surface to form a CoSi$_2$ ring, in vigorous competition with the silicidation process occurring at the buried interface, and thus giving rise to the volcano feature of the pinholes [Fig. 2(b)]. In general, the surface morphology depends strongly on the Co coverage and the annealing temperature. At lower coverage, pinhole generated islands do not form an enclosure while at high coverage the islands associated with neighboring pinholes are coalesced, both making it difficult to identify the unique process described here.

The driving force for the Si outward diffusion is clearly due to the free Co atoms on the outer surface. However, diffusion channels would have to be activated to allow the Si atoms to rush to the surface in mass, which results in the pinhole morphology. This is a rapid thermal process and cannot be studied by our present setup. Nonetheless, our result suggests that inhibiting these diffusion channels through some means may very well be a more effective way to eliminate pinholes in CoSi$_2$ processing. Indeed, we speculate that this could be the main reason behind several successful fabrication schemes such as the interrupted co-deposition and the template mediated growth, all yielding a CoSi$_2$ film with little or no pinholes. Detailed in situ microscopic characterization and especially real time studies of the growth kinetics may help to bring this long-standing problem to a close.

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FIG. 2. (a) A 1.5 μm×1.5 μm STM image of a 20 CoSi$_2$ on Si(111) obtained by post-room-temperature-deposition annealing at 580 °C. The Co coverage is ~5 Å. The depth of the pinholes (dark patches) varies from 20 to 50 Å while the opening ranges between 400 and 1500 Å. (b) A 8500 Å ×5500 Å STM image of a pinhole enclosed by a elevated bank of CoSi$_2$, forming a volcanolike feature.

38 Å of Si. From the comparison of theoretical value of \( V_{\text{CoSi}_2}/V_{\text{Si}} \) with the measurement of \( V_{\text{island}}/V_{\text{hole}} \), we conclude that the Si atoms excavated from the pinholes are responsible for building up its surrounding CoSi$_2$ ring. The small discrepancy may reflect the inability of the STM to

FIG. 3. The correlation between the volume of pinholes and the volume of the respective surrounding islands. The solid line is a least square fit to the data in filled triangles. A ratio of ~0.9 indicates that Si atoms removed from pinhole are consumed in the surrounding island.