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A Novel Technique for Ultrathin $CoSi_2$ Layers: Oxide Mediated Epitaxy

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I. Abstract

The novel technique of oxide mediated epitaxy (OME), recently described for the growth of single crystal $CoSi_2$ layers on the (100), (110), and (111) surfaces of silicon is presently demonstrated on narrow (0.22μm) Si lines and on implanted p^+ and n^+-Si. Deposition of a thin layer of cobalt (1-3nm) onto Si surfaces covered with a thin peroxide-grown SiO_x layer and annealing at 500-700°C led to the growth of essentially uniform, epitaxial, $CoSi_2$ layers, independent of the orientation, the geometry, or the doping level of the Si. On all surfaces, thicker (10-30nm), excellent quality, $CoSi_2$ single crystal thin films were grown by repeated growth sequences.

II. Introduction

The formation of reliable, low-resistance, shallow, silicide contacts to Si metal-oxide-semiconductor field effect transistors (MOSFET) with < 0.18μm design rule is still a significant challenge. In addition to its resistivity, the uniformity and the thermal stability of the silicide contact layer are also important for device applications, as any layer non-uniformity or tendency to agglomerate weakens or threatens the junction integrity. Of the three silicides ($CoSi_2$, $TiSi_2$ and NiSi) with low bulk electrical resistivities, $CoSi_2$ is particularly attractive because (1) it is easy to form on narrow Si lines, (2) it can be used as a dopant diffusion source, and (3) it can form epitaxial structures because of a good lattice matching condition with Si. The desire for epitaxial silicide lies in their smooth interfaces, excellent layer uniformities and high thermal stabilities.[1)] Epitaxial $CoSi_2$ layers can be grown by molecular beam epitaxy (MBE) on clean Si surfaces.[1)] On Si(100), however, MBE growth of single crystal $CoSi_2$ layers requires some forms of Si deposition and, hence, is not a self-aligned process. The Ti-interlayer mediated epitaxy (TIME) scheme[2)] is capable of fabricating high quality $CoSi_2$ layers on blanket, undoped Si(100). TIME, however, suffers from the formation of large voids in the epitaxial $CoSi_2$ layers near the edges of field oxide,[3)] the formation of $CoSi_2$ with multiple orientations on heavily arsenic doped Si, and an inability to grow uniform epitaxial $CoSi_2$ layers with thicknesses of less than 40nm.[4)] Thus, it appears that the oxide mediated epitaxy (OME) technique recently reported[5-6)] is the only technique which is capable of generating, in a self-aligned fashion, high quality epitaxial $CoSi_2$ layers with thicknesses of less than 30nm.

III. Results and Discussions

The OME process employed Si substrates which were first submerged in a hot peroxide-containing solution for a few minutes so that the surface was covered with a thin layer of SiO_x. The exact composition of the solution did not seem to much affect the OME effect as both acidic and alkaline solutions were shown to work.[5)] The OME technique utilized the observations that $CoSi_2$ grew epitaxially on peroxide-treated Si surfaces and that no epitaxial growth occurred on atomically clean Si surfaces, when the thickness of the deposited Co layer exceeded 2nm. One well-known exception[1)] was that on Si(111) epitaxial growth of $CoSi_2$ occurred even when the surface was atomically clean. Shown in Fig. 1 are channeling and random RBS spectra of a ~ 40nm thick epitaxial $CoSi_2$ layer grown from the depositions of 2nm Co, 9nm* $CoSi_{0.7}$, and 2nm Ti at room temperature onto a peroxide-treated Si(100) and an anneal at 730°C for 2 minutes in nitrogen. (A 1nm* $CoSi_x$ layer denotes one which contains the equivalent of 1nm Co and that amount of Si which makes for the specified composition ratio.) Very good channeling characteristics were observed, in spite of the low annealing temperature. On atomically clean Si(100), the same deposition and annealing sequence led to the growth of a polycrystalline $CoSi_2$ layer. The thin SiO_x layer was clearly crucial to the success of the OME phenomenon.

From deposited layers of pure Co, it was shown that within an optimum thickness range of ~ 1-3 nm Co, entirely epitaxial and essentially continuous $CoSi_2$ layers could be grown on the (100), (110) and (115) surfaces of Si after an anneal at ~ 550-700°C. Outside of this thickness range, $CoSi_2$ layers either are discontinuous or contain non-epitaxial grains.[5)] Auger analyses suggested that the thin SiO_x layer originally resided on the Si surface remained largely on the surface and covered the epitaxial $CoSi_2$ layer after the anneal. Epitaxial $CoSi_2$ was the only reacted phase positively identified in the entire OME process using <3nm Co, with an onset temperature for the formation of $CoSi_2$ of ~ 460°C. One should keep in mind, however, that the difficulties with the detection of phases and the short reaction time of phases in films of such small thicknesses might obscure the detection of transient phases. Nevertheless, that $CoSi_2$ was apparently the first nucleated silicide phase was recently proposed to be explained by a limited supply of metal (Co) to the growth interface and a decrease in the effective metal concentration.[7)]

High quality epitaxial $CoSi_2$ layers grown from pure Co were limited to ~ 11nm in thickness in one deposition sequence (1nm Co reacts with ~ 3.6nm Si to grow ~ 3.6nm $CoSi_2$). Thicker layers could be grown by using the thin OME-grown $CoSi_2$ layers as templates. Deposition of a thin layer of Co on the surface of a thin OME-grown $CoSi_2$ epitaxial layer at room temperature and annealing at 600-750°C were shown to effectively increase the thickness of the $CoSi_2$ layer without affecting the epitaxial orientation of the layer. Repeated deposition and annealing cycles were also used to demonstrate the growth of thick, 20-30nm, single crystal $CoSi_2$ layers with nearly perfect crystallinity. The high-temperature deposition method,[8] previously demonstrated for template growth of $NiSi_2$ layers, was found unreliable for the OME process because of the re-evaporation of cobalt.[6] Co re-evaporation was clearly attributable to the presence of the thin surface SiO_x layer over the epitaxial $CoSi_2$ layer.[6] Thick, epitaxial $CoSi_2$ layers grown from OME template layers were of high structural quality. Faceting at the as-grown $CoSi_2$ layers could be significantly reduced by a high temperature anneal, as shown in Fig. 2, driven by a minimization of the interface energy.

When 1-3nm Co was deposited on the peroxide-treated (111) and (112) surfaces of Si, annealing at 550-650°C led to the growth of $CoSi_2$ films with two epitaxial orientations. The majority of $CoSi_2$ layers grown under these conditions on Si(111) had type B oriention, but a high density of small type A oriented $CoSi_2$ grains were also present. On Si(211), the majority of the films had type A orientation, but small type B oriented grains were also included in the films. When the template technique was applied to the thin OME layers grown on (111) and (112), type A oriented areas were observed to expand. Type A grains grew at a faster rate and eventually take over the type B oriented regions because of the poor mobility of type B interface.[9] Typically, after one deposition and annealing sequence on (112) OME-grown template layers, entirely type-A oriented $CoSi_2$ layers were grown. On Si(111), the transformation of mixed A-B $CoSi_2$ into pure type A orientation was slower and less reproducible. Essentially (>99%) type A oriented $CoSi_2$ could be grown, but only after three repeated deposition and annealing sequences. Previously observed formation of pinholes in type B $CoSi_2$ layers on Si(111) was absent in the present experiment, likely because the present $CoSi_2$ surface was covered with a thin oxide cap which removed the thermodynamic driving force for pinhole formation, namely, a transition in surface structures.

OME grown $CoSi_2$ layers on heavily implanted (5E15 As 50keV or 5E15 BF_2 50keV, 850°C/30min) Si(100) were also of high qualities. Shown in Fig. 3 were channeling and random RBS spectra taken from a 18nm thick $CoSi_2$ layer grown on As-implanted Si, using the template method. Singly-oriented $CoSi_2$ was observed. Interestingly, the usual surface peak of arsenic were absent, as shown in the glancing angle spectra of Fig. 3(a). Most As was repelled from the $CoSi_2$ lattice, leading to a possible pile-up at the interface and also some minor As loss, as shown in Fig. 3(b). OME growth on patterned Si(100) proceeded much like that on blanket Si. Near the edges of a 100nm thick field oxide layer, a 18nm thick $CoSi_2$ layer showed no evidence for layer non-uniformity, as shown in Fig. (4). A 13nm thick $CoSi_2$ layer grown by OME and template methods on narrow, 3E15 As implanted, single-crystal Si lines, separated by polysilicon lines and SiO_2 spacers, was found to be single crystalline and continuous, as shown in Fig. 5. The narrowest single crystal Si lines on the test pattern shown in Fig. 5 had width of 0.22μm. Even though the OME effect was presently demonstrated mainly with evaporated Co, low power sputtering of Co in high purity Ar gas was also expected to show similar epitaxial growth, as preliminary results indicated.[10] It thus appeared that the fabrication of shallow epitaxial $CoSi_2$ contact by OME was compatible with self-aligned formation and compatible with conventional processing environments. There could even be potential applications for OME processes similar to that shown in Fig. 1. The effect of the inclusion of a small amount of Si in the deposits on the ability for self-aligned formation was largely unknown.

The success of the OME process depended on the cleanliness of the deposited cobalt film, as air exposure was shown to impede the epitaxial growth. However, oxygen from the SiO_x layer, which came in contact with the deposited cobalt layer, did not impede the OME growth. These results were suggestive that Co did not react chemically with the SiO_x layer, but rather diffused through the thin oxide layer and reacted directly with the Si crystal. The weak structure of the peroxide-grown SiO_x layer likely facilitates such a diffusion more efficiently than a dense, high-integrity, SiO_2 layer would. A thicker SiO_2 layer (~ 5nm) was previously shown to lead to the growth of polycrystalline Ti silicide layers with higher thermal stability.[11] The ability of Ti to react with SiO_2 chemically was deemed important for the observation of silicide reaction in that work. Indeed, a thin layer (2nm) of stoichiometric SiO_2 was observed to block the Co silicide reaction at the usual OME temperatures.[5] Therefore, the enhanced epitaxy of $CoSi_2$ in the OME seemed not to be directly related to the presence of the SiO_x. However, the presence of the SiO_x might have created circumstances which aided the nucleation or the growth of silicide with the epitaxial orientation. For example, the presence of the SiO_x layer could have impeded volume change or grain rotation associated with the nucleation/growth of some (non-epitaxial) silicide phases or orientations. The SiO_x layer could also have changed the nucleation conditions of silicide by changing (at least on one side) the interface energy of the nuclei. It actually would be more appropriate to attribute these atomistic mechanisms to the other major function the SiO_x layer serves, namely, a cap to the silicide reaction, rather than to attribute them to SiO_x the diffusion barrier. Since the stability of a silicide thin film depended on interface and surface energetics, capping by SiO_x was crucial to the good layer uniformity of OME grown $CoSi_2$. Since there was no clear chemical role played by the SiO_x in assisting the epitaxial growth of $CoSi_2$, it was likely that the thin SiO_x layer/cap could also aid the reaction in other silicide forming epitaxial or non-epitaxial systems. The epitaxial system of $NiSi_2$/Si was an obvious choice for OME to be observed.

IV. Conclusions

In summary, OME growth of high quality epitaxial $CoSi_2$ was demonstrated for various Si surface orientations, narrow Si lines, and heavily doped surfaces. A thin SiO_x layer grown by peroxide treatment on the Si surface was crucial to the attainment of epitaxial silicide growth. The importance of this SiO_x layer "capping" the silicide reaction was also pointed out. Thicker (20-30nm), excellent quality $CoSi_2$ layers were also grown by OME and template techniques. No major obstacles to the application of the OME technique in device fabrication were discovered.

V. References

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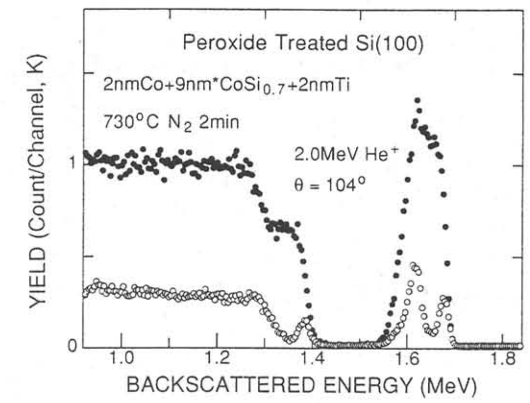
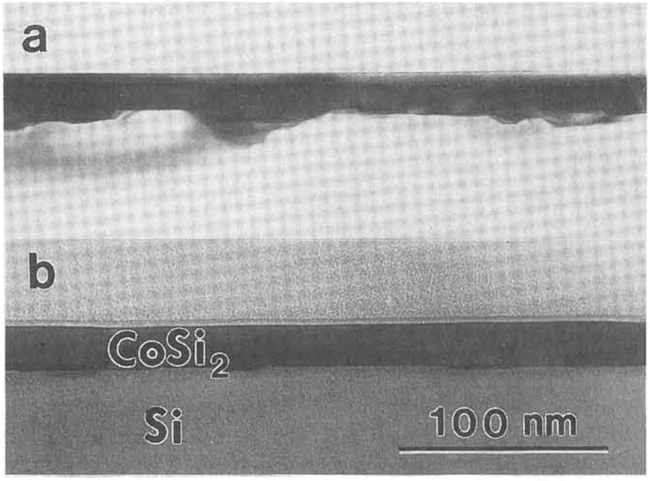


Fig. 1. Channeling and random 2MeV He^+ RBS spectra of a ~ 39.6nm thick $CoSi_2$ layer, grown by depositions of 2nm Co, 9nm* $CoSi_{0.7}$, and 2nm Ti on oxidized Si(100), and an anneal at 730°C in N_2.



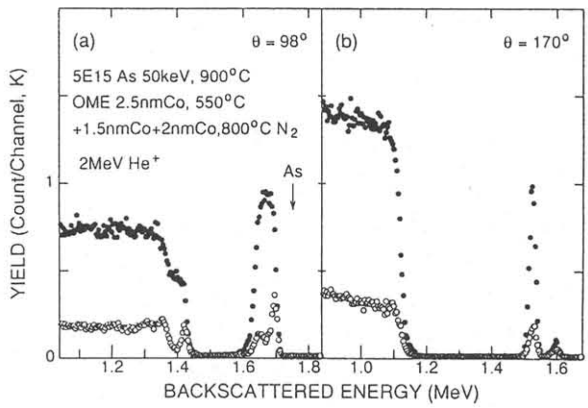
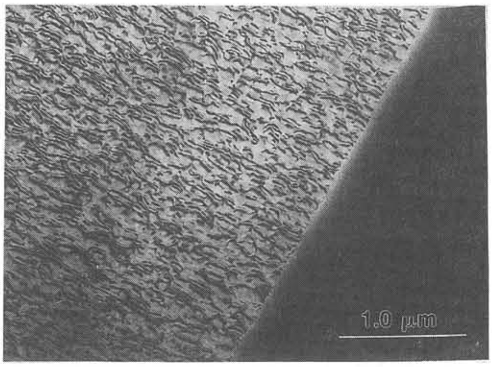


Fig. 2. (above left) Cross-sectional TEM images of (a) a 18nm thick $CoSi_2$ layer grown by OME and template techniques on Si(100) at 730°C. (b) same layer after a 850°C 20min anneal in N_2.
Fig. 3. (above right) Channeling and random 2.0MeV He^+ RBS spectra from a 18nm thick $CoSi_2$ layer grown on As-implanted Si(100) by OME and template methods, using (a) glancing angle detector for better depth resolution, and (b) backscattering detector for mass separation.



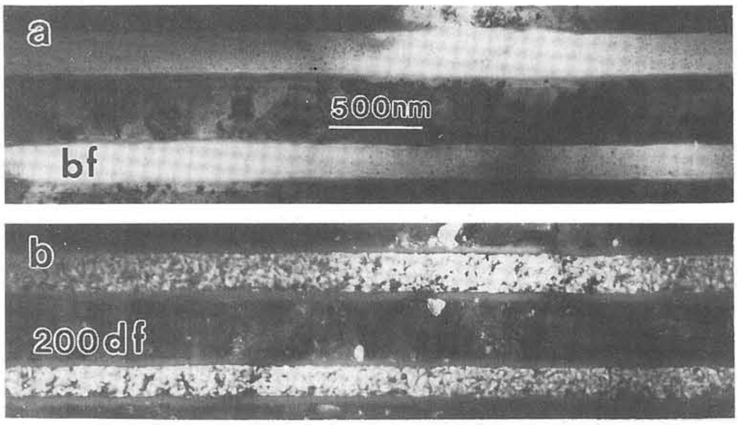


Fig. 4. (above left) Planview, bright-field, TEM image of a 18nm thick $CoSi_2$ layer grown by OME and template methods on Si(100), near the edges of a 100nm thick field oxide layer.
Fig. 5. (above right) Planview (a) bright field and (b) (200) dark-field TEM images of a 13nm thick $CoSi_2$ layer grown on an As-implanted Si(100) wafer. Epitaxial $CoSi_2$ (light-colored lines) was grown on single crystal Si lines using OME and template techniques. On the $8nmSiO_2/150nm$ poly-Si gate stack, polycrystalline $CoSi_2$ was grown. 80nm thick SiO_2 spacers were used.