Epitaxial Growth and Electrical Properties of Thick $SmSi_2$ Layers on (001) Silicon

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Received November 30, 2009; accepted December 7, 2009; published online February 22, 2010

We report on the growth of thick (up to 1.2 μm) epitaxial samarium disilicide layers on (001) oriented silicon substrates. The films have the bulk tetragonal $SmSi_2$ structure and composition, and grow with a preferential orientation $SmSi_2$[100] ∥ Si[110]. A surface reconstruction transition from (1×1) to (2×2) appears below ~525 °C. Transport measurements show an n-type metallic conduction with a room temperature resistivity of 175 μΩ cm decreasing to 85 μΩ cm at 4 K, and a carrier concentration of 1.3×10^{22} cm^{-3}. © 2010 The Japan Society of Applied Physics

DOI: 10.1143/JJAP.49.025505

1. Introduction

The potential to form silicides, and especially epitaxial silicides, as elements of Si-based integrated circuitry has attracted attention for some decades. The rare earth silicides (RESi) are especially attractive for their metallic nature and their very low Schottky barrier heights of 0.3–0.4 eV (0.7–0.8 eV) on n-type (p-type) silicon.[1–5] They have application potential for low-resistivity metallic contacts, rectifier diodes, and infrared detectors.[3,4,6] More recently their propensity to form nanostructures[7–9] and their promise for a new generation of interconnects and contacts in very large scale Si-based integrated circuits[10,11] has sparked renewed interest in RESi films.

Previous studies of epitaxial RESi utilized mainly (111) oriented silicon substrates, where the films grow with ordered Si vacancies to form RE_3Si_5 ($RESi_{\sim 1.7}$) with an hexagonal AlB_2 structure, encouraged by the 6-fold symmetry and close lattice match between the two structures.[1,4] The growth of Sm on Si(111) in the monolayer range has received particular attention, due to the propensity of Sm to change from divalent to trivalent with increasing coverage.[12–14] However, with the aim of integrating RESi in the mainstream of silicon based micro-electronics, the Si(001) oriented substrate is preferred. Several papers have focussed recently on the formation of hexagonal RESi self-assembled nanostructures on Si(001),[7,9,15] including observations that the formation of Sm_3Si_5 nanowires or three dimensional (3D) islands with the hexagonal bulk structure is controlled by the substrate vicinality.[8,16] However, only limited attention has been devoted to the epitaxial growth of thick RESi layers on this face,[5,17–21] and there appear to be no reports of the growth of bulk samarium-silicide layers on Si(001). Here we report the growth, structure, and electrical properties of especially high-quality epitaxial $SmSi_2$ layers up to 1.2 μm thick, prepared by evaporating the samarium directly onto hot silicon (001) substrates, so-called reactive deposition epitaxy.

2. Results and Analysis

The experiments were performed on nominal ±0.5° Si(001) substrates in a Thermionics ultrahigh vacuum system ($<10^{-8}$ Torr). Sm metal was evaporated from a tungsten wire basket, and the evaporation rate monitored by a quartz-crystal thickness monitor. The layer thickness was verified by scanning electron microscopy and Rutherford backscattering spectrometry (RBS). The substrates were prepared by thermal outgassing at ~600 °C for 2 h in the growth chamber, and then the native oxide was removed by annealing at ~950 °C. Reflection high-energy electron diffraction (RHEED) along the [110] Si azimuth showed the appearance of the (2×1) surface reconstruction corresponding to monoatomic steps [Fig. 1(a)], indicating clean and well-ordered surfaces. The growth temperature and rate were adjusted to optimise the rapid two-dimensional (2D) growth mode of the $SmSi_2$ layer, achieved with a temperature above 500 °C, and a Sm evaporation rate less than 0.2 nm/s. All of the films described here were grown under these conditions. The RHEED pattern evolution during the direct growth on Si indicated that an initial 3D growth mode progressively becomes 2D after 10–20 nm. Figure 1(b) shows the RHEED pattern observed after the formation

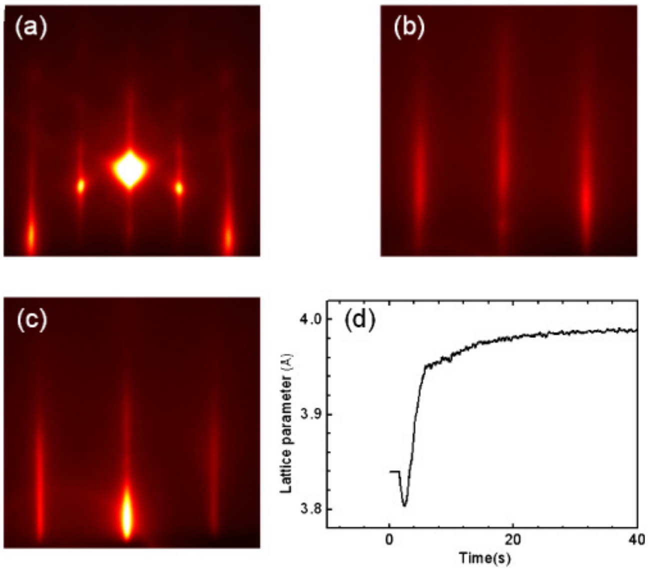

Fig. 1. (Color online) RHEED pattern evolution along the Si[110] azimuth: (a) clean Si(001) surface showing a (2×1) surface reconstruction prior to deposition, (b) after 50 nm, and (c) after 250 nm of $SmSi_2$. (d) Evolution of lattice parameter as a function of time during the early growth stages.

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of 50 nm of $SmSi_2$ at 600 °C. By increasing the thickness of the $SmSi_2$ the diffraction streaks become sharper and more intense [Fig. 1(c)], indicating a very smooth, flat surface.

The in-plane lattice parameter deduced from the RHEED pattern along the Si[110] azimuth is 4.03 Å, in agreement with the value observed in the high-temperature tetragonal structure of bulk $SmSi_2$ (4.041 Å).[22] Furthermore the diffraction patterns along the Si[100] azimuth show streak separations $\sqrt{2}$ larger than along [110], clearly indicating that the $SmSi_2$[110] azimuth lies along Si[100].

Thus the $SmSi_2$ lattice grows with a 45° rotation relative to the Si substrate lattice; the epitaxial growth of single crystalline $SmSi_2$ films is achieved with a preferential orientation $SmSi_2[100] \parallel Si[110]$ on silicon (001) substrates. Such a rotation by 45° with respect to the Si(001) plane reduces the lattice mismatch from +25.6 to −5.2%, as has also been reported for the growth of orthorhombic $GdSi_2$,[23] tetragonal $DySi_2$,[17] or hexagonal $LuSi_{1.7}$ layers.[18]

The lattice parameter variation deduced from the RHEED pattern taken along Si[110] is shown as a function of the growth time in Fig. 1(d). After an early stage where the lattice parameter decreases, further growth allows a rapid relaxation of the $SmSi_2$ lattice. About 80% of the initial strain is relaxed within tens of nanometers. The remaining compressive residual strain is then relaxed over the next 250 nm of growth.

Decreasing the temperature after the growth, a faint diffuse (2×2) surface reconstruction along the $SmSi_2$[110] azimuth appears at about 525 °C and the resulting pattern becomes very sharp and intense at room temperature (RT). Increasing the substrate temperature reverses the reconstruction sequence at the same temperatures. Figure 2 shows the horizontal profile of the diffracted intensity for RHEED patterns taken from a 300 nm thick film at 600, 525, and 430 °C. The RHEED pattern images at the growth temperature [Fig. 2(a)] and RT [Fig. 2(b)] are displayed also.

It has been reported that rare earth silicides form when the rare earth deposition is carried out at temperatures as low as 350 °C,[24–27] prompting us to grow also at reduced temperatures. Deposition onto a previously-formed epitaxial $SmSi_2$ layer did indeed lead to further $SmSi_2$. However, we do not observe the (2×2) surface reconstruction in films grown below a temperature of 350 °C, and the RHEED pattern is three dimensional. Note that the complete transformation of the Sm layer into a $SmSi_2$ layer may no longer occur in these films without subsequent annealing; our experimental data are unclear on this point.

Bulk $SmSi_2$ is recognised to undergo a tetragonal to orthorhombic transformation[28,29] at about 380 °C but we have seen no evidence of that in our RHEED patterns. Note, however, that the contrast between the *a* and *b* axes of the orthorhombic phase is very small, approximately 1%, and thus below the resolvable limit set by the widths of the RHEED features.

Figure 3 displays the XRD 2θ-scan of a 1.2 µm thick $SmSi_2$ layer. We see that only the (00l) lines are observed over the entire angular range, which is expected for tetragonal epitaxial films grown on (001) oriented substrates. The implied lattice constant along the growth axis is found to be 13.32 Å, in agreement with the expected bulk value of 13.3 Å.[22] The full width at half maximum of the $SmSi_2$(004) peak deduced from the XRD rocking curve is about 0.23°. An XRD ϕ-scan of the (001) $SmSi_2$ plane (not shown) indicates a 4-fold symmetry, characteristic of an in-plane cubic structure. We note that XRD measurements do not show significant variations in bulk structure and strain across the growth temperature range, from 350 to 700 °C. In particular, we did not observe a phase transformation by increasing the temperature, as reported for the Gd–Si system (from hexagonal to orthorhombic).[30,31]

Using RBS the Sm/Si ratio is found to be 1 : 2 within ±5%, independent of film thickness ranging from 250 nm to 1.2 µm. The ratio does not vary significantly from the interface to the surface, in contrast to reports for $ErSi_{1.7}$ layers.[32] These results show that at temperatures around 600 °C the interdiffusion of Sm and Si atoms which induces the disilicide formation permits full mixing to a depth of at least 1.2 µm, without the appearance of significant Si vacancies.

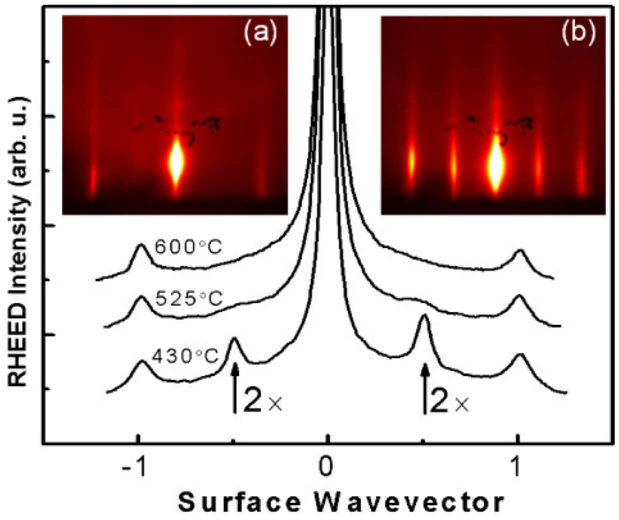

Fig. 2. (Color online) Horizontal profile of RHEED intensity taken at 600, 525, and 430 °C along the $SmSi_2[1\bar{1}0]$ azimuth. Insets: RHEED pattern images at (a) growth temperature, and (b) room temperature. Note that the RHEED screen defects apparent in the images, developed after the results shown in Fig. 1, do not influence the intensity plotted in the main figure.

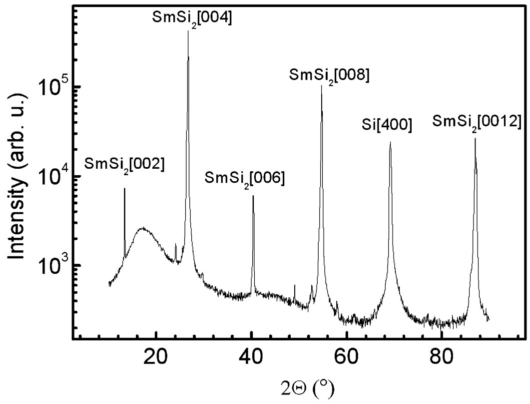

Fig. 3. XRD 2θ-scan of a 1.2 µm thick $SmSi_2$ layer showing only the [00l] reflections as expected for epitaxial tetragonal $SmSi_2$ grown on (001) oriented substrates.

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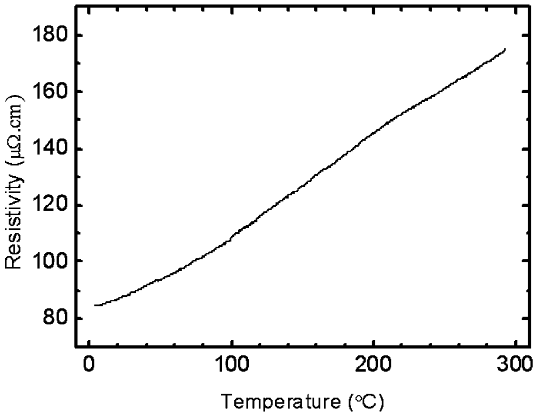

Fig. 4. Temperature dependent electrical resistivity of a 300 nm thick $SmSi_2$ layer.

Electrical transport was investigated by resistivity measurements conducted from RT down to 4 K, and Hall effect measurements were carried out at fields from 0 to 8 T. The 0.25 mm thick, 10 Ω cm Si substrates did not affect the resistivity measurements, but they introduced significant contamination to the measured Hall coefficient at high temperature and low fields. Thus carrier concentrations were determined at 70 K using fields above 1 T. The results show n-type carrier concentrations of 1.25 (±5%) × 10^{22} cm^{-3} at 70 K, with no dependence on film thickness. The high-field limit at 300 K indicate the same carrier sign and concentration within ≈30%. Previous reports of silicides have shown both n- and p-type conduction,2,33) with carrier concentrations on the order of 5 × 10^{21} cm^{-3}.

The temperature-dependent resistivity shown in Fig. 4 is clearly metallic. Films from 300 to 1.2 μm thick showed the same temperature dependence, and the same absolute magnitude to within the 5% uncertainty in their thicknesses. The residual resistivity $\rho_{4K} = 85\,\mu\Omega\,cm$ is comparable to the intrinsic phonon-limited resistivity $\rho_{in} = \rho_{300K} - \rho_{4K} = 90\,\mu\Omega\,cm$, indicating a moderate level of disorder scattering. The intrinsic resistivity is somewhat larger than found in other rare earth silicides; previous reports have shown $ErSi_2$ with 44 μΩ cm,33) and $ErSi_{1.7}$ with 24 μΩ cm,2) whilst $GdSi_2$ has been reported to have $\rho_{in} = 34\,\mu\Omega\,cm$,33) and $GdSi_{1.7}$ $\rho_{in} \approx 54\,\mu\Omega\,cm$.34) There is no evidence of an anomaly that might signal a magnetic ordering temperature as has been reported for $ErSi_2$, $GdSi_{1.7}$, or $DySi_{2-x}$.2,17,34) The relatively high carrier concentration and low intrinsic conductivity suggests an effective mass and/or electron–phonon interaction somewhat higher than in $ErSi_2$ and $GdSi_2$, but the mobilities inferred from the data are similar to those found in various transition metals. It is unclear at the moment whether this larger resistivity would impact on the potential of $SmSi_2$ as an electrical contact.

3. Summary

In summary, we have shown that tetragonal and stoichiometric $SmSi_2$ layers can be grown onto (001) oriented silicon substrates by reactive deposition epitaxy, with the films oriented $SmSi_2$[100] ∥ Si[110]. The films have metallic type conduction with a low resistivity and a higher n-type carrier concentration than those reported for other RESi. Such an epitaxial $SmSi_2$-based layer may prove very useful for further studies of the integration of RESi in silicon-based microelectronics.

Acknowledgment

The authors are grateful to A. Hyndman, G. Williams, and M. Ryan for rocking curve and phi-scan measurements. The research reported here was supported by a grant from the New Economy Research Fund (contract VICX0808).

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