Bulk versus Surface Transport of Nickel and Cobalt on Silicon

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We compare directly the rates of bulk versus surface transport for Ni in and on Si(111) by depositing a laterally confined dot of Ni on one side of a double-polished and UHV cleaned Si wafer and then measuring the lateral Auger profile on the reverse side following annealing and quenching. Ni reaches the far side of the wafer at temperatures as low as 550 °C via bulk diffusion with no measurable contribution from surface paths, which are short circuited by numerous, fast bulk paths. Similar results are found for Ni and Co on Si(111) and Si(100). Implications for silicide reactions in general are described.

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The role of diffusion in thin film reactions has been much studied, especially for silicide-forming contact reactions in which a metal cold deposited on silicon is annealed to induce a reaction. Activation energies in the vicinity of 1.5 eV are found for transition metal atoms diffusing through a silicide film [1]. Reaction kinetics are less well characterized for more recent silicide growth schemes such as mesotaxy and low temperature molecular beam epitaxy (MBE) [2,3]. Conventional wisdom holds that diffusion along free surfaces or interfaces is much faster than through bulk, with the result that net mass transport through a defective film is generally dominated by "short circuit" paths. Indeed, for simple metals the activation energy for grain boundary diffusion is typically half that for lattice diffusion [4], and for surface diffusion it is even smaller [5]. The question therefore arises as to the role of surface diffusion in the various silicide growth schemes. Here we show that the conventional wisdom is inverted in the case of Ni and Co on clean Si surfaces, in that fast bulk diffusion acts to short circuit slow or nonexistent surface diffusion. Thus these metals dissolve into bulk silicon without spreading across a clean surface. This result has significant implications for silicide reactions.

Si samples were cut from double polished, 0.2 Ω cm P-doped wafers, then cleaned *in situ* by heating to 1200 °C, which produced a 7 × 7 reflection high-energy electron diffraction (RHEED) pattern on both sides of the wafer and no trace of contamination in Auger scans. Metal was deposited by sublimation from a high purity (5*N*) wire. Thickness was calibrated *in situ* with a crystal thickness monitor and *ex situ* by ion scattering for a net accuracy of 15%. Temperatures above 700 °C were measured with an optical pyrometer while lower temperatures were determined by interpolation of heating power curves. Auger signals were measured with a single pass cylindrical mirror analyzer with a lateral resolution of 0.2 mm FWHM.

We first attempted to measure surface diffusion directly via edge-spreading Auger profiles of Co deposited on Si(111). Upon annealing from 200 to 920 °C, however, the Co Auger signal simply disappeared (passing through a sequence of silicide phases) without spreading at all. Yet it could be restored by quench cooling and the edge profiles could then be measured at room temperature. The results are shown in Fig. 1 for various times of anneal at 920 °C. These profiles are not erfc curves that one would expect for a typical diffusion experiment, but rather they show a plateau (imposed by the bulk solubility limit, as described later) followed by a sharp drop. We found that the leading edge of the profiles moved as $\sqrt{t}$, and from this we extracted a diffusivity of $D = 1 \times 10^{-4}$ cm^2 sec^{-1}. This compares with a bulk value of $D = 3 \times 10^{-5}$ cm^2 sec^{-1} [6]. Similar results have been reported by Dolbak *et al.* for Ni [7]. The interpretation of such experiments, however, is questionable since the contribution to the Auger signal from surface island formation, bulk precipitates, and/or sublimation of metal is unknown. Hence we explored the quench process more fully, as described below.

Ni was chosen for the quench experiments rather than Co because its solubility in Si is much higher [6]. Ni was deposited at room temperature in steps of 0.05 monolayer

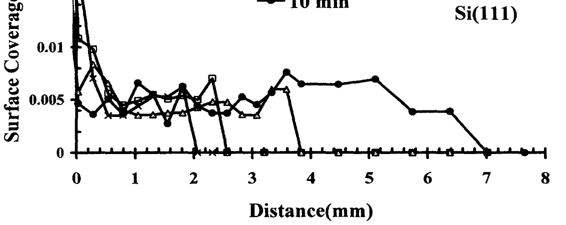

FIG. 1. Edge-profile measurement of diffusion for Co on Si(111) at 920 °C, with surface concentration determined from the Co *LVV* Auger signal.

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(ML). Then Auger and RHEED were measured for each step after annealing to 1000 °C for 10 sec and quenching, with an initial cooling rate of approximately 100 °C/sec. The results are shown in Fig. 2. Establishing the coverage dependence of the RHEED patterns allows us to monitor the metal coverage on both sides of the wafer for the diffusion experiment (below). The 7×7 reconstruction is extinguished at a surface coverage of 0.05 ML (vertical axis), leaving a 1×1 pattern. The 1×1 structure consists of a variable density lattice gas of so-called ring clusters and has been named the (1×1)-RC phase [8,9]. The well-known $(\sqrt{19} \times \sqrt{19})R$ 23.4° pattern begins to form at 0.10 ML and is fully formed at 0.20 ML. Since the (1×1)-RC phase coexists with the $\sqrt{19}$ phase it is difficult to accurately determine the intrinsic coverage of the latter. Our results favor an intrinsic coverage near $3/19 = 0.16$ ML, corresponding to 3 Ni atoms per $\sqrt{19}$ unit cell. We have elsewhere described an atomic model for this structure based on scanning tunneling microscope (STM) observations [10]. At much higher coverage, islands of B-type $NiSi_2$ are formed, which produce a transmission diffraction pattern and distinct Kikuchi bands showing the B-type orientation [11].

We note that the submonolayer phases appear simultaneously on the top and bottom surfaces of the wafer indicating that the Ni is fully equilibrated through the wafer thickness during the anneal. Furthermore, we find that exactly half of the cumulative Ni dose is restored to the surfaces (both top and bottom) by the quench. This behavior is indicated by the solid line in Fig. 2 and holds well for surface coverages below 0.2 ML. It is significant that no Ni remains in the bulk following the quench. Within the accuracy of our data, the remaining bulk concentration "n" is less than 0.02 ML/wafer thickness, or $n < 3 \times 10^{14}$ cm^{-3}. Thus the surface segregation process is highly effective, aided both by the fast bulk diffusivity and thermomigration due to the vertical temperature gradient during the radiation quench [12]. For surface coverages above 0.2 ML we presume that surface Ni saturates the submonolayer phases and begins to form 3D islands with thickness larger than the Auger escape depth. Such islands have been observed under similar conditions using UHV scanning electron microscopy and low energy electron microscopy (LEEM) [7,9].

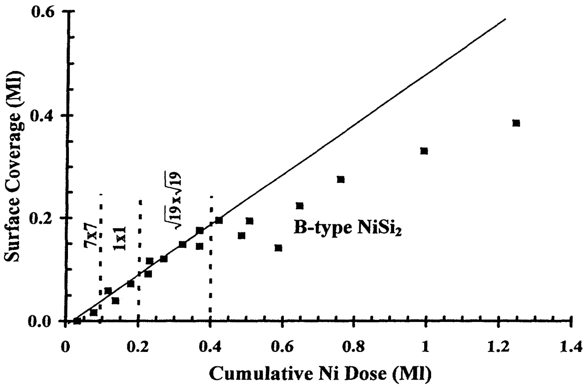

FIG. 2. Surface coverage (Ni LVV Auger signal) vs cumulative dose of Ni following anneal and quench steps. Dotted lines mark the points where the RHEED pattern changes, as indicated. Solid line indicates a surface coverage equal to half the cumulative dose.

The edge-profile experiments suggest that surface transport of Ni or Co on Si actually takes place via bulk paths. Yet it is difficult to rule out the contribution of surface paths to net mass transport in such experiments and to accurately calibrate diffusivity measurements for comparison with known bulk values. Hence we devised the following direct comparison or "race" between surface and bulk transport processes. A small dot (20 Å thickness and 0.5 mm diameter) of metal was deposited on the back side of a double-polished UHV-cleaned wafer. The sample was annealed at 850 °C for 10 sec then quench cooled and lateral scans of Auger on the reverse side and RHEED on both sides of the wafer were performed. The results are shown in Fig. 3 for Ni/Si(111). The fact that the Auger concentration of Ni is peaked at the center of the wafer directly opposite the source shows clearly that metal atoms reached the far side via bulk, not surface, paths. A similar curve was obtained in the "long direction" parallel to the heating current, indicating that current induced migration is negligible on this scale.

The RHEED patterns on both the top and bottom of the wafer were 1×1 near the center and 7×7 near the edges where the Ni concentration was below 0.04 ML, in agreement with the coverage dependence shown in Fig. 2. From the discussion above we know that the quench process restores all of the bulk-dissolved Ni to the surfaces (top and bottom). Thus we interpret the quenched Auger signal to represent the lateral profile of the depth-integrated (from the wafer midplane to the respective surface) bulk concentration present at the end of the diffusion-anneal step. The solid line is a model

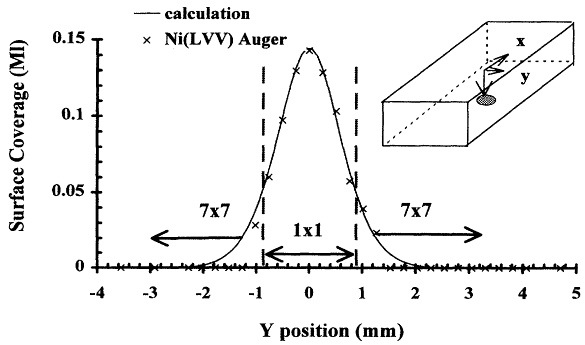

FIG. 3. Lateral scan of Ni LVV Auger signal on the far side of the wafer, opposite the Ni source following an anneal at 850 °C for 10 sec and a radiation quench.

calculation corresponding to a hemispherical error function convoluted with a disk-shaped source then depth integrated and broadened with a Gaussian resolution function for the Auger probe. The fit is optimized with values of diffusivity $D = 1 \times 10^{-4}$ cm^2/sec and solubility $S = 1 \times 10^{16}$ atom/cm^3. D and S are fully decoupled, since the width of the curve is affected only by D. The fitted values are close to the literature values for Ni in Si at 850 °C [6] as shown in Table I. Similar results were obtained for Ni/Si(100) and for Co/Si(111) and (100), also shown in Table I. Because of solubility limitations, Co required a somewhat higher temperature anneal, and Ti yielded no surface signal at all.

Before declaring a winner in the race of bulk versus surface transport we first need to clarify the "rules" of the race. It should be noted that we measure flux, not diffusivity alone. The relevant physical parameters can be understood in a simple one-dimensional geometry [13]. Thus the surface concentration of metal atoms that reach the far side via bulk diffusion in the direction "z" is given by $N_b/A = \int_{z=zo/2}^{zo} C_b^{(0)} \operatorname{erfc}(\xi_b)\, dz$, where $\xi_b = z/2\pi\sqrt{D_b t}$ and $C_b^{(0)}$ is the bulk solubility (N/cm^3). The analogous quantity for surface diffusion along "x" is given by $N_s(x)/A = C_s^{(0)} \operatorname{erfc}(\xi_s)$, where $\xi_s = x/2\pi\sqrt{D_s t}$ and $C_s^{(0)}$ is the surface solubility (N/cm^2). The shape of the Auger profiles indicate no measurable level of N_s/A. Therefore, we cannot separate $C_s^{(0)}$ and D_s, so either parameter could limit the surface flux. To our knowledge there are no measurements of $C_s^{(0)}$ in the literature for transition metals on Si surfaces. However, our LEEM observations of the (1×1)-RC phase suggest that monolayer levels of Ni or Co atoms are mobile at temperatures near 800 °C [9]. This suggests that indeed D_s is limiting the flux. Next we need to discuss possible extrinsic limitations to surface diffusion [14]. First, Ni atoms may sublimate from the surface. This does not occur, since Ni dissolves instead, as shown in Fig. 2. Second, extrinsic defects such as surface steps may inhibit surface diffusion. This is ruled out because we know there is adequate flux diffusing through the entire wafer thickness. Hence, transport under a single surface step could not be rate limiting. Finally, a high temperature anneal would favor bulk over surface diffusion if its activation energy were higher. We find that Ni passes through the Si wafer at temperatures as low as 550 °C, below which the Auger signal is unmeasurable due to limited bulk solubility. In other work, we have shown using STM that the diffusivity of Co on Si(111) is bulklike at 320 °C [15].

TABLE I. Values of diffusivity and solubility obtained from through-wafer lateral Auger profiles for various systems and temperatures. Literature values, taken from Ref. [6], are given in parentheses.

System	T (°C)	D (10^{-6} cm^2 sec^{-1})	S (10^{14} cm^{-3})
Ni/Si(111)	850	100 (20)	100 (300)
Ni/Si(100)	750	9 (10)	10 (60)
Ni/Si(111)[a]	550	⋯ (3)	3 (1)
Ti/Si(111)[b]	1000	⋯ (10^{-5})	⋯ (10^{-2})
Co/Si(111)[c]	920	100 (30)	3 (1)

[a] Annealed to steady state, hence no lateral profile obtained.
[b] No signal at all obtained.
[c] Derived from the top-surface edge profile in Fig. 1.

In summary, we have shown that mass transport for Ni or Co on Si(111) or Si(100) occurs via bulk diffusion with no detectable contribution from surface diffusion. This will likely be true for all late transition metals in silicon and could be described as the result of there being for these metals numerous (due to high solubility), fast ($Q \sim 0.5$ eV) bulk interstitial diffusion paths that short circuit the surface paths. In addition, metal atoms in these systems are strongly bound with high coordination number in "ring-cluster" structures [8] and do not simply hop between surface adsorbtion sites. The situation for early transition metals, such as Ti, is less clear. In this case, bulk paths are virtually cut off due to extremely low bulk solubility. However, surface solubility is also apparently very small, since there are no surface phases known for Ti/Si. In this case it would be difficult to detect surface diffusion using macroscopic methods such as Auger.

These results have some bearing on silicide reactions, as mentioned in the introduction. In conventional contact reactions metal (or silicon) diffuses through polycrystalline silicide, whereas in our experiment metal diffuses through single crystal silicon, so these processes are not directly comparable. Nonetheless, surface-interface diffusion along grain boundaries is thought to dominate the mass transport in contact reactions. However, the observation of grain boundary decoration following reaction may simply reflect surface-interface segregation upon cooling [16]. Explicit tests of surface versus bulk diffusion using single crystal silicides would be informative. Low temperature MBE by codeposition of metal and silicon has been used to fabricate nearly perfect epitaxial CoSi$_2$ overlayers [3]. In light of our results, one might question whether surface diffusion plays any role at all in this process. In the mesotaxy method near perfect epitaxial layers of CoSi$_2$ buried in Si are formed by rapid thermal annealing of implanted Co [2]. In this case, crystal growth is dominated by diffusion processes exactly analogous to those we have measured (i.e., metal diffusing through single crystal silicon). Thus the near perfect plate geometry of the buried silicide is not caused by fast surface-interface diffusion, but rather must be a growth shape that occurs via bulk mass transport alone.

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