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Published in:
Surface Science

DOI:
10.1016/S0039-6028(98)00481-6

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1998

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Diffusion, nucleation and annealing of Co on the H-passivated Si(100) surface

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Received 25 March 1998; accepted for publication 29 May 1998

Abstract

We investigate the diffusion, nucleation and annealing behaviour of Co on H-passivated Si(100) surfaces by scanning tunneling microscopy (STM). Due to the absence of nucleation sites for silicide formation, the nucleation and growth mode is dominated by the formation of non-epitaxial islands which merge by increasing Co coverage. The island number density $N$ shows a power law dependence on coverage $h$ ($N \propto h^{3.0 \pm 0.05}$) for room temperature deposition. Annealing at temperatures up to $\sim 400^\circ$C results in small changes of the Co clusters, while deposition at elevated substrate temperatures ($\sim 400^\circ$C) results in the formation of fewer but coarser Co islands. Finally, at higher annealing temperatures ($\sim 490^\circ$C) where H desorption takes place, the formation of two-dimensional islands occurs which are surrounded by an irregular $2 \times n$ ($n > 1$) reconstructed surface due to interstitial diffusion of Co into Si. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Growth, Nucleation, Scanning tunneling microscopy, Surface relaxation and reconstruction

1. Introduction

Although the presence of surface impurities is nearly unavoidable in thin film growth, the introduction of the right impurity in the film/substrate interface (surfactant) can greatly improve the morphology of thin films [1–11]. Indeed, recent works have demonstrated that the introduction of certain impurities as adsorbates during film deposition can improve various film characteristics (growth mode, interfacial roughness and/or surface roughness) [1–12]. An understanding of the impurity effect is eventually important in order to control a given growth process at an atomic level. Hydrogen is a commonly used impurity in Si-type growth process, and its adsorption on a surface is often advantageous or unavoidable during processing (e.g. in chemical vapour deposition from gas-phase precursors like SiH$_4$). It has been shown that in homoepitaxial Si/Si(100) growth, surface roughening rate, epitaxial thickness (H reduces the critical thickness for epitaxial growth or completely interrupts epitaxy depending on H coverage), and island size depend significantly on H coverage [13–19]. In Al film growth, H is known to influence film growth rate, nucleation, and thin film texture [20–24].

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PII: S0039-6028(98)00481-6
has been demonstrated by Adams et al. [25]. By contrast, in the heteroepitaxial Ge growth on Si, H can improve interface abruptness by suppressing intermixing or mediate layer-by-layer growth by nominally flat (miscut H wet-passivated Si(111) surfaces [12], the better than room temperature (RT) nucleation study of Co atoms on H-passivated Si(100) surfaces [12]. The reconstructed Si(100)2×1 surface did not contain Si adatoms which constitute the nucleation sites for Co-silicide even at RT [30,31]. The elimination of these nucleation sites leads to three-dimensional clusters in the early stages of deposition, indicating that nucleation of highly reactive thin metal films can be strongly altered by the presence of adsorbates in the Co/Si interface. Presumably, the nucleation sites on the H-passivated surface are surface defects (e.g. steps, impurities or some other flaws) [12], or just statistics (if two or more metal atoms meet they form immobile clusters) [23–25].

Although for industrial applications the Si(100) surface is more relevant, the growth of CoSi2 on this surface is more complex. The difficulty stems from the multiple possibilities of the CoSi2 structure on Si(100), where besides the desired (100) orientation the growth of (110) and (112) misoriented grains occurs [32–35]. Up to now, the nucleation properties of Co on H-passivated Si(100) surfaces, as well as the annealing behaviour of Co islands in the presence of H (for temperatures where H starts desorbing and silicidation occurs), still remains widely unexplored. This will be the topic of the present work. Finally, we note that also for future STM nanostructuring (in a manner described recently for Al and Fe [23–25]), the knowledge of nucleation and silicidation of Co atoms in the presence of H is required.

2. Experimental procedure

The Si(100) wafers used in this study were nominally flat (miscut <0.1°), p-doped with resistivity ~30 Ω cm. The sample preparation was performed in a UHV chamber of base pressure \( P_b = 1 \times 10^{-10} \) mbar. Clean Si(100)2×1 reconstructed surfaces were formed by resistive heating. After degassing to ~750°C at a pressure ~3 \times 10^{-15} \) mbar, they were subsequently flashed to ~1200°C for ~10 min followed by a rapid switch to 750°C, and multiple short flashings to ~1200°C until the pressure sustained below 10^{-9} \) mbar for more than 30 s. Specimen temperature was determined by infrared pyrometry to better than ±10°C above 400°C.

The reconstructed Si(100)2×1 samples were dosed with atomic H from high purity \( H_2 \) which was dissociated at a hot (~1500°C) W-filament that was placed at a distance of ~8 cm from the sample. The latter was kept at a temperature of ~400°C to ensure monohydride coverage. The \( H_2 \) was supplied by a leak valve that was placed 40 cm from the W-filament. The passivations lasted 6 min at a chamber pressure \( P_{H_2} \approx 3 \times 10^{-3} \) mbar resulting in a dose of approximately 1080 L (1 L = 10^{-6} Torr s) which suffices to passivate fully the Si(100)2×1 surface by a monohydride termination layer [36–38]. On a 25 × 25 nm² scan area of a H-passivated Si(100) surface about 10 defects are found which lead to a defect density of \( \sim 1.6 \times 10^4 \) defects/μm².

The Co films were deposited on the H-passivated Si(100) samples (~1.5 h after H-passivation for the Si substrate to be equilibrated at RT) by means of e-beam evaporation at a rate 0.0017 nm/s unless otherwise noted. The latter was calibrated by a quartz crystal microbalance to within ~10% error. One monolayer (ML) is defined as 1 ML = 6.8 × 10^{14} cm² which corresponds to the Si atom density on the Si(100) surface. During evaporation the chamber pressure did not exceed ~3 × 10^{-9} \) mbar. Finally, in all stages the samples were imaged in situ into an STM (OMICRON) at a pressure of ~1.5 × 10^{-10} \) mbar. Finally, mechanically cut Pt/Ir STM tips were used for imaging and patterning purposes.
3. Results and discussion

Upon submonolayer deposition of Co onto a bare Si(100)\(2 \times 1\) surface at RT, the formation of almost parallel ribbons of dimer row sections occurs (Co-induced reconstruction), for which a possible explanation might be the interstitial diffusion of Co atoms into Si [39,40]. We sometimes see a vacancy ordering at RT which is attributed to sample contamination (from Ni or Co) and does not increase significantly upon RT deposition of Co on H-Si(100). The reconstruction was found to be unaffected by the Co coverage in the range 0.01–2 ML, and substrate temperature during deposition in the range RT–600°C [40]. Moreover, Co adatoms will react with Si forming islands on top of the Si surface.

3.1. Behaviour at temperatures prior to H desorption

Upon deposition of Co onto a fully H-passivated Si(100) surface, since the preferred sites for nucleation are removed and barriers to lateral diffusion are reduced (Si dangling bonds are passivated with H), it is expected that a behaviour completely different from bare Si(100) will develop. Indeed, deposition of 0.067 ML of Co at RT (Fig. 1) leads to the formation of round shaped Co islands which nucleate on terraces. In between the islands, the substrate \(2 \times 1\) reconstruction appears to be intact, which implies that few of the hydrogen atoms are displaced by diffusing Co monomers or dimers. Moreover, interstitial diffusion of Co atoms into Si is clearly prohibited by the H termination layer, since otherwise indications of the Co-induced reconstruction would be present even at RT [40].

The majority of the Co islands have lateral size \(d \approx 1–3\) nm, and maximum height \(\sim 0.25\) nm (hexagonal phase), we can infer from the island heights that they are at most two layers high. The average distance between the islands is of the order of \(\sim 1–5\) nm, which suggests a significant diffusion length (at this deposition rate) of the incoming Co adatoms prior to coalescence larger than \(\sim 2\) nm. Enhanced metal adatom surface mobility is a common theme on H-passivated Si surfaces for a wide variety of other systems which include Ag, In, Cu, and Al [23,26–29]. We note that the formation of row-like islands perpendicular to the substrate dimer rows is rarely observed in Fig. 1.

Fig. 2 shows that upon annealing the film shown in Fig. 1 at 405°C, the H-passivation layer around the Co islands does not degrade, neither is any interaction of the Co islands with the substrate observed, which would manifest itself as Co-induced reconstruction as a first sign of such a reaction. This is consistent with the fact that H starts desorbing at \(\sim 470°C\) [41]. The annealing treatment does not alter drastically the RT grown Co clusters, which implies that the already formed clusters are rather immobile after their formation. Moreover, any ripening effects (evaporation from islands) are absent since the average island size still remains in the range \(\sim 1–3\) nm. This is not surprising if one takes into account that Co has a rather elevated melting temperature of 1495°C.

3.2. Deposition at elevated temperature

We will compare the nucleation of Co deposited onto a heated substrate with that at RT. Fig. 3A
shows a Co/H/Si(100) film formed at RT upon deposition of 0.2 ML of Co, while Fig. 3B shows a film formed at 400°C substrate temperature with the same coverage. Indeed, the coverage was chosen significantly high in order to reveal the temperature effect more efficiently in comparison with that formed at RT. In Fig. 3B vacancy ordering is observed which signals Co interstitial diffusion as discussed above. Such a reaction can occur since at elevated temperatures H is somewhat mobile [15] and apparently displaced by diffusing Co atoms. Nevertheless, the H termination layer blocks significantly such a reactive process.

Furthermore, at 400°C an enhanced diffusion of the incoming Co atoms occurs which is reflected with the formation of a few laterally large islands of size ~5 nm and maximum height ~0.3 nm. The distance in between the islands can be as large as 10–20 nm, which suggests diffusion lengths larger than ~10 nm. The observed small islands (~1 nm in size) in between the large ones are presumably Co and surface defects (depassivated dangling bonds), as comparison with empty state images (positive substrate bias voltage) reveals. The formation of large islands as in Fig. 3B by deposition at elevated substrate temperatures (above 300°C) has also been observed in earlier nucleation-diffusion studies of homoepitaxy of Si on Si(100), and was attributed to an island coarsening mechanism [42, 43].

3.3. Behaviour at temperatures where H desorption occurs

Since processing at elevated temperatures is in many cases unavoidable in device fabrication, it is
important to understand how metal atoms behave upon annealing at temperatures where H starts desorbing. Annealing the film shown in Fig. 2 at 490 °C for 5 min, H desorption occurs which results in strong reaction of the Co atoms with the underlying Si. This is manifested in two distinct ways. The first is the interstitial diffusion of Co into Si which leads to deterioration of the Si(100)2 × 1 reconstruction into the Co-induced reconstruction (Fig. 4) [40]. The second involves the formation of row-like islands on top of and perpendicular to the Si dimer rows as depicted clearly in Fig. 4. We analyse both features below.

Due to the interstitial diffusion, the Si(100)2 × 1 row structure is reordered by row ribbons and trenches of missing dimers running perpendicular to the Si dimer rows. Although similar behaviour has been observed for deposition of Co on bare Si(100) [40], in the present experiment the reconstruction appears to be more irregular, especially in the vicinity of the observed islands, with a quasi-periodicity 2 × n with n ~ 4–9. At this temperature range Co must have formed silicide, as for example UPS studies have shown CoSi₂ formation to occur at ~ 500 °C [44].

The shape of the two-dimensional islands varies from single row to roughly rectangular. The width to length ratio of the two-dimensional islands in Fig. 4 varies between 0.1 and 0.5, which is similar to ratios found in the growth of Co deposited onto heated bare Si(100) substrates at 500 °C [40]. The apparent island height of ~0.12 nm is comparable to the step height of the Si(100) surface (0.136 nm), and the interlayer spacing of the CoSi₂ structure (0.134 nm). Si-terminated islands are energetically preferred because the surface free energy of Si is significantly lower than that of Co [45]. Also, at this temperature CoSi₂ [44] forms, and the two possible CoSi₂ structures that occur on Si(100) are Si-terminated [45]. Hence, we expect that the observed islands will be Si-terminated with the Co atoms underneath the top Si layer, in agreement with previous studies on bare Si(100) [40].

Finally, further annealing of the film shown in Fig. 4 at 522 °C (where H desorption peaks) leads

![Fig. 4. Annealed Co/H/Si(100) film of Fig. 1 at 490 °C for 5 min. Filled state image (scan size 80 nm) acquired at −2.0 V bias voltage and current 0.1 nA. Two-dimensional islands are formed which are surrounded by Co-induced reconstructed areas.](image1)

![Fig. 5. Annealed film of Fig. 4 at 522 °C for 30 s. Filled state image (scan size 30 nm) acquired at −2.0 V bias voltage and current 0.1 nA. The two-dimensional islands still survive the heat treatment.](image2)
to further deterioration of the Si reconstructed surface (Fig. 5). The two-dimensional islands on top still survive the annealing treatment in this temperature range.

3.4. Dependence on coverage

The coverage dependence of the Co islands is depicted in Fig. 6 where mainly the density increases, without any significant increment in height with increasing Co coverage $\theta$. In all cases, we do not observe any preferential nucleation of Co on step edges, but instead mainly on substrate terraces. Direct counting of islands from the images yielded number island densities ($N$) for the four coverages shown in Fig. 6 with a power law dependence $N = 0.234 \theta^c$ with $c = 0.29 \pm 0.03$ (Fig. 7). This is consistent with random nucleation theory which predicts (for slow deposition rate and low coverage) the coverage dependence of the number island density $N \propto (3R/D)^{1/3} \theta^{1/3}$ with $R$ the deposition rate and $D$ the diffusion coefficient [42,43]. This relation is based on a two-dimensional isotropic random walker model of the incoming adatoms on the surface.

The agreement of the measured exponent $c = 0.29 \pm 0.03$ with the random walker model prediction $c = 1/3$ is somewhat surprising given that the vacancies are present, and we have already approached a regime with significant coverage. The vacancies are shown in the STM images to be unpopulated with Co atoms, leading effectively to deviations from the random walker model. Indeed, we point out that in all cases shown in Figs. 1–3 and 6 there is no clear correlation of the islands with the surface vacancies, with which any interaction is rather unknown. Indeed, the deposited adatoms do not fill preferentially vacancies, indicating that these surface defects do not represent perfect adatom traps. However, it will not be

![Image](https://via.placeholder.com/150)

**Fig. 6.** Coverage dependence of the Co islands deposited at RT with increasing coverage: (A) 0.022 ML, (B) 0.067 ML, (C) 0.13 ML, and (D) 0.2 ML, respectively. Filled state images (scan size 40 nm) acquired at bias voltage $\sim -2.1$ V and current $\sim 0.12$ nA.
to Al [23], the random walker model for Co on H-passivated Si(100) cannot be simply compared with results of Co on bare Si(100), since in that situation there is not only a different sticking coefficient, but also interstitial diffusion leading to drastic alteration of the bare surface (Co-induced reconstruction) [40]. Fig. 8 shows the dissimilar nature for growth on bare and H-passivated surfaces. The STM tip is used to define depassivated lines (~7–8 nm wide) by electron stimulated H desorption (patterning parameters: tip current 5 nA, bias voltage 7 V, writing speed 300 nm/s) [36–38], and subsequently Co is deposited at RT. The formed Co/Si nanowires have an effective width of ~7–8 nm showing a nanometer scale control over feature size, and have a rather compact structure which is different from the isolated Co islands on the H–Si(100) surface (further details will be given elsewhere) [47].

Finally, from the inset of Fig. 7 which shows $N^3$ vs. deposition time $t$, a linear fit is used to estimate the diffusion coefficient $D$ from the slope assuming the validity of the random walker prediction: slope $\propto 3R^2/D$.

Fig. 7. (a) Log-log plot of the island number density versus Co coverage which yields a slope 0.29 close to the value 1/3 predicted from the model of an isotropic adatom random walker. The actual fit gives $\ln(N) = -1.45 + 0.29 \ln(t)$. (b) Plot of $N^3$ vs. deposition time $t$, and a linear fit to estimate the diffusion coefficient $D$ from the slope assuming the validity of the random walker prediction: slope $\propto 3R^2/D$.

The actual fit gives $\ln(N) = -1.45 + 0.29 \ln(t)$. (b) Plot of $N^3$ vs. deposition time $t$, and a linear fit to estimate the diffusion coefficient $D$ from the slope assuming the validity of the random walker prediction: slope $\propto 3R^2/D$.

Fig. 8. 0.13 ML of Co deposited on a patterned H-passivated Si(100) sample at RT. Filled state image (scan size 50 nm) acquired at bias voltage $-2$ V and current 0.12 nA.
$D = 1.49 \times 10^{-11} \text{cm}^2/\text{s}$. Moreover, we assume an Arrhenious behaviour $D = D_0 e^{-E/RT}$ to describe two-dimensional surface diffusion [15,42,43,46] with $E$ an activation energy, and $D_0 \approx v_{a2}^2/4$ [46] with $v \sim 10^{13} \text{Hz}$ a typical vibrational frequency and $a_0$ the lattice spacing ($a_0 = 0.251 \text{nm}$). Substituting this leads to an activation barrier for diffusion of the incoming particles $E \sim 1.2 \text{eV}$ at RT. Such a value of the activation barrier is rather high and comparable to estimated diffusion barriers of Si on Si(100) surfaces partially dosed with H [15].

Acknowledgements

This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie" (FOM) which is financially supported by the Nederlands Wetenschappelijk Onderzoek (NWO). This work is supported by the ESPRIT research program 22953 CHARGE. G.P. would also like to acknowledge useful discussions with G. Backx, T.-C. Shen, and J.W. Lyding.

4. Conclusions

In summary, we have investigated the effect of complete hydrogen passivation on the formation of Co islands on Si(100) surfaces. Due to the fewer nucleation sites for silicide formation on the passivated surface, the nucleation and growth mode is dominated by the formation of non-epitaxial islands which show a power law dependence of the island number density on Co coverage. $N \sim a^{-0.25}$ for RT deposition. This is close to the predictions of an isotropic random walker model of the deposited adatoms, where possible deviations might be due to the presence of vacancies which appear unpopulated with Co atoms. In addition, the impinging Co adatoms do not nucleate preferentially at step edges. An estimation of the diffusion coefficient and the activation energy gave $D \sim 1.49 \times 10^{-11} \text{cm}^2/\text{s}$ and $E \sim 1.2 \text{eV}$ respectively.

Upon annealing at $\sim 400^\circ \text{C}$ little change is observed in the Co islands while the H-passivation layer remains intact around the islands. However, deposition of Co onto heated substrates leads to the formation of fewer but coarser Co islands. Finally, upon annealing at higher temperatures exceeding the hydrogen desorption temperature (470 $^\circ \text{C}$), Co–Si bonding occurs. This is manifested by the reconstruction due to the fast interstitial diffusion of Co in Si, and the formation of two-dimensional islands possibly Si-terminated with the Co atoms underneath. Annealing at higher temperatures leads to further deterioration of the silicide islands and the surface structure.

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