

Patterning of Si(100): Spontaneous Etching with Br₂

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Atomic resolution scanning tunneling microscopy of Si(100)-(2×1) shows that terrace patterning is possible during etching under tuned conditions of Br fluence and temperature. This patterning reflects the coordinated breaking of dimer bonds with redimerization that produces rows of Si doubly bonded to Br adjacent to Si dimers singly bonded to Br. The concerted desorption of the SiBr₂ units yields a missing row pattern.

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Si(100) etching has been termed “spontaneous” if secondary ionization or exposure to electron and photon beams is not needed [1]. Modeling of this process emphasizes adsorption and diffusion so that volatile species are formed randomly on the surface [2–5]. In this case, terrace patterning does not occur, although step etching and retreat are possible [6]. An alternate and very intriguing process can be envisioned in which the surface concentration is sufficiently high that ordered domains of mixed volatile and nonvolatile species could be formed dynamically followed by coordinated desorption of the volatile species. The possibility of forming domains derived from mixed-bonding configurations is suggested by studies of H-Si(100)-(2×1) where rows of Si atoms doubly bonded to H alternate with rows of dimerized Si with single bonds to H [7]. For H-Si, these bonding configurations are not volatile [7], but their existence suggests that analogous geometries might be achieved with the chemically similar halogen atoms. Figure 1 shows this alternating bonding character. For the halogens, one might expect spontaneous removal of the volatile doubly bonded species so that rows of Si dimers would alternate with rows of missing Si atoms. In this Letter, we provide direct evidence of this type of patterned removal of rows

of Si atoms from Si(100)-(2×1) during spontaneous etching with Br₂.

The results shown here were obtained using Si(100) wafers oriented within 0.5° of (100). Experiments with wafers having greater terrace widths also showed terrace patterning. The wafers were rinsed in ethanol prior to introduction into a vacuum chamber that housed the scanning tunneling microscope. They were degassed overnight at 600°C and flash heated to 1200°C. The pressure was below 4×10^{-10} Torr during flashing. This procedure resulted in ordered Si(100)-(2×1) with low defect densities [8,9]. An electrochemical cell was used to provide Br₂ at a constant flux, with the current through the cell serving as a direct measure of the Br release [10]. Under our experimental conditions, a fluence from the source of 1.5 mAs produces a monolayer (ML) of Br on Si(100) at 300 K where 1 ML = 6.98×10^{14} atoms cm⁻² (Ref. [6]). In all cases, samples were rapidly cooled to room temperature immediately after shutting off the Br₂ source.

Figure 2 shows a $\sim 400 \times 400 \text{ \AA}^2$ occupied-state scan-

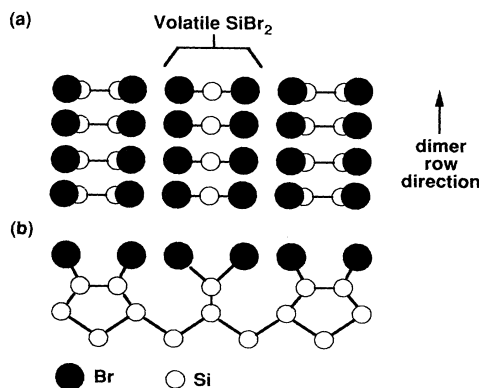


FIG. 1. (a) Top view and (b) side view of the proposed 3×1 Br-Si structure showing the volatile SiBr₂ units which, upon desorption, yield the patterned surface with missing atom rows.

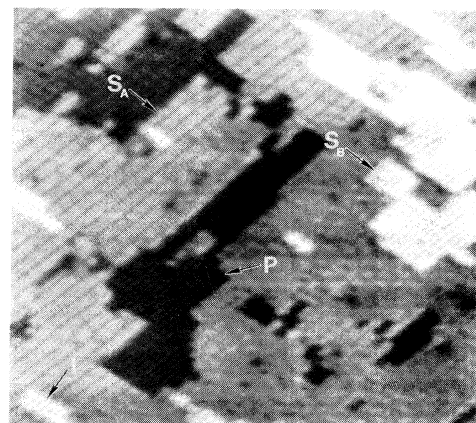


FIG. 2. Occupied-state STM image of Si(100)-(2×1) after 1.8 mAs Br at 900 K ($\sim 400 \times 400 \text{ \AA}^2$, -2 V , 0.2 nA). Terrace etching produces one-atom-layer deep etch pits, labeled *P*. Si atoms freed during etching form one-atom-layer high Si regrowth islands, *I*.

ning tunneling microscopy (STM) image obtained after exposure to 1.8 mAs Br at 900 K. This is typical of the early stages of etching at 900 K, not the steady state conditions [6]. The two-domain nature of the surface with dimer rows running in orthogonal directions on adjacent monatomic steps is evident. Terrace etching has resulted in the formation of Si regrowth islands, denoted *I*, and etch pits that are one atom layer deep, marked *P*. Even in the presence of Br, Si atoms have maintained the growth characteristics of Si atoms on bare Si(100) [11]. Si regrowth islands, thus, are highly elongated along the perpendicular direction to the substrate dimer rows. Most of the etch pits are rectangular in shape and are elongated in the dimer row direction because of preferential etching parallel to the dimer rows [6]. Their widths generally exceed 2 dimers. Under these conditions, rectangular peninsulas are also etched into the characteristics S_A and S_B steps [6]. Despite this etching, the surface shows ~ 0.9 ML of adsorbed Br, including that on the regrowth islands, singly attached to the dimer atoms and preserving the 2×1 geometry of the substrate. We focus here on the transformation from this etching morphology to patterning of the terraces.

Figure 3 shows that the surface morphology changes when the Br fluence is increased by ~ 0.2 to 2 mAs. While etch pits are still present, missing rows that are a single atom wide have appeared on the terraces. In some regions, the missing atom rows, denoted MR, alternate with dimer rows to produce a domain with a 3×1 structure, as outlined. In principle, some of the MRs could result from Si regrowth, constituting domain boundaries [11], but the large number density and the fact that etching occurs at 900 K indicate that regrowth plays a minor role here. The etching mechanism that produced Fig. 2, namely, the nucleation and growth of etch pits aided by high Br mobility [6], is still operational but it cannot explain the missing row morphology.

Exposure to a higher fluence of Br at constant flux resulted in an increased number of missing atom rows, the

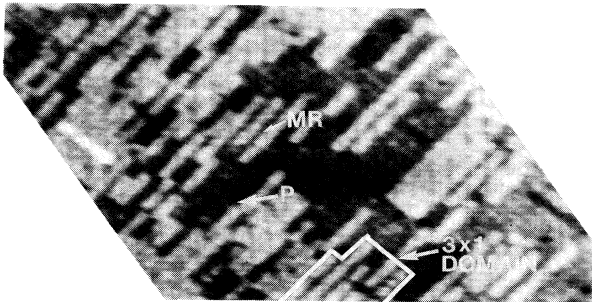


FIG. 3. Drift-corrected occupied-state STM image after exposure to ~ 2.0 mAs Br at 900 K ($\sim 300 \times 300 \text{ \AA}^2$, -1.7 V, 0.1 nA). Missing atom rows (MR) have appeared. They alternate with dimer rows to form small domains of a 3×1 structure.

steady state morphology being dominated by 3×1 domains. Figure 4(a) shows a steady state surface obtained after ~ 2.4 mAs. The process of concerted etching is evident from the outlined 3×1 domain. The width of the missing atom rows appears larger in the domain in the upper right due to drift in the image. Figure 4(b) shows a high resolution occupied-state image of the surface represented by Fig. 4(a). An alternating arrangement of the dimer rows and the missing atom rows is clearly evident. The dimer portion of the outlined 3×1 unit shows two bright features with a central depression. This is indicative of Br bonding since dimers on clean Si(100) exhibit central maxima in occupied-state images [12]. Each bright feature corresponds to a Si-Br bond, the dimer being a (SiBr)₂ dimer. Reversing the sample-tip bias to obtain unoccupied-state images produced no change in structure.

Estimates of the amount of Br remaining after expo-

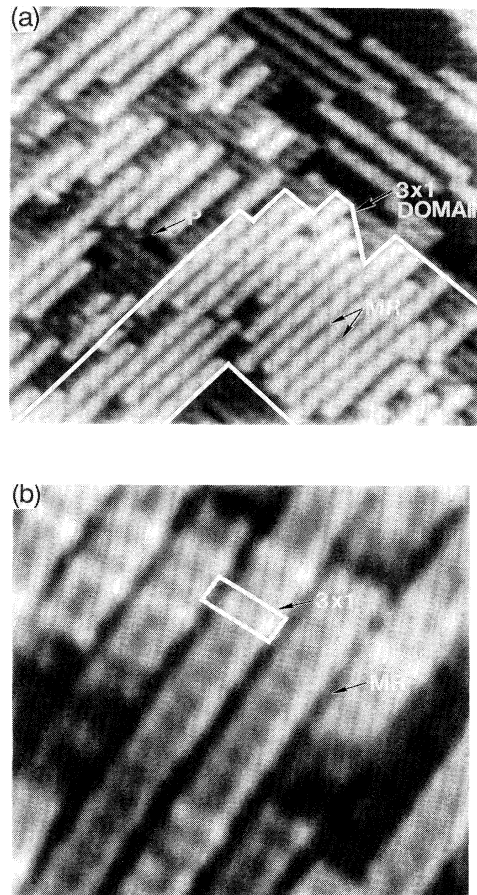


FIG. 4. (a) Occupied-state image after ~ 2.4 mAs Br at 900 K ($\sim 230 \times 230 \text{ \AA}^2$, -1.8 V, 0.05 nA) where patterning dominates. (b) Smaller scale image where the 3×1 unit cell of the missing row structure is outlined. The atomic resolution of the dimers indicates one Br atom bonded to each Si atom.

sure provide an indirect assessment of the etching efficiency. For fluences below 1.8 mAs, the STM images show a continuous increase in the amount of residual Br. In particular, etching with ~ 0.4 , 1.2, and 1.8 mAs leaves ~ 0.1 , 0.3, and 0.9 ML of Br adsorbed on the surface. This trend is broken after ~ 2.0 mAs, represented by Fig. 3, when the amount of residual Br abruptly drops to ~ 0.7 ML and the 3×1 structure appears. This indicates that patterned etching consumes some of the Br that otherwise remains in an adsorbed state. Such a process translates into enhanced SiBr_2 formation since SiBr_2 is the dominant etch product at 900 K [4]. While indicating that the missing atom rows result from SiBr_2 desorption, this analysis does not explain the ordering of the rows in the first place. However, insight into the dynamics of the 3×1 missing row morphology can be obtained by comparison to H-Si(100).

Hydrogen adsorption at 400 K under saturation conditions produces a 3×1 structure that has alternating SiH_2 monomers and SiH dimers [7]. This converts to a 2×1 structure with SiH units when H is lost upon heating to 600 K. Conversely, H addition to the 3×1 structure at 300 K yields a 1×1 structure with only SiH_2 bonding [7]. Theoretical studies have rationalized these phase transformations based on the coverage of H [13]. Thus, the 2×1 phase is thermodynamically stable for coverages up to 1 ML but converts to the 3×1 phase for 1–1.33 ML and then saturates in the high density 1×1 phase. Predictions for the F-Si(100) system yield similar results for coverage-dependent phase changes [14]. Although no ordered phases have been observed for F-Si(100) [15], this could be due to significant reaction with Si backbonds at 300 K, even for coverages of ~ 0.5 ML [1]. For Cl-Si(100) [3] and Br-Si(100) [16], only the 2×1 structure is observed below ~ 1 ML. An extension of the H-Si(100) trend would suggest the 3×1 to be the next stable geometry. The fact that the patterned 3×1 structure appears after ~ 0.9 ML Br is observed on the surface indicates the formation of this metastable structure and a coverage-dependent phase transition.

Analysis of the unit cell of Fig. 4(b) demonstrates that a SiBr dimer alternates with a missing Si atom. We propose that the etch patterns result from a 3×1 Br-Si(100) adsorption phase, as for H-Si, but that desorption of the volatile SiBr_2 species creates a missing Si row. The structure prior to desorption is sketched in Fig. 1.

Further investigations show that patterning depends on the fluence but not the flux since images similar to those shown were obtained at 900 K with a quarter and twice the flux. None exhibited 3×1 domains until ~ 1.8 mAs. Thereafter, they became common and the morphology of Fig. 4(a) was reached after ~ 2.4 mAs. The coverage dependence of patterning can be understood by noting that exposure first produces a 2×1 configuration with Br singly bonded to Si. Here we see that the addition of Br to a surface that is $\sim 90\%$ SiBr bonded induces a transformation to the 3×1 phase. Such ordering is driven by

the local rather than global Br concentration so patches are formed and etching proceeds from them. This would expose the next Si layer, would lead to a redistribution of Br, and would curtail the patterning process until it is reactivated by Br addition. Since the surface concentration depends on the fluence, the phase change and the onset of patterning should be largely independent of flux or the time to reach the local critical coverage, as observed.

Finally, the temperature dependence of patterned etching shows that it is possible only in a narrow temperature window between 850 and 900 K. This was established by exposing Si(100) surfaces to a fluence of ~ 2.4 mAs at temperatures between 300 and 1000 K. In addition, a surface dosed with ~ 3.0 mAs at 300 K was imaged after stepwise heating to 1000 K. In both cases, we found no evidence of the 3×1 structure below 850 K but patterning was evident for those treated at 850 or 900 K. Exposure above 900 K did not allow sufficient Br accumulation for the surface to undergo the 3×1 transformation. The need for high temperatures to attain the 3×1 phase reflects the fact that the structure would involve extensive bond breaking and coordinated redimerization. For H-Si, this can be done at much lower temperature since H is able to break the dimer bonds, even at room temperature [7]. Again, annealing after an initial dose of only ~ 0.5 ML at 300 K failed to yield a 3×1 pattern since the critical coverage was never achieved.

This paper has demonstrated that models of etching must include the dynamics of a high-coverage surface. In particular, it will be a challenge to model the coordinated formation and desorption of SiBr_2 rows and examine the stability of dimer rows produced at 900 K. Certainly, the presence of Br on the dimer rows plays an important role in their persistence. Significantly, the process of spontaneous etching results in patterning of the terraces and produces structures that cannot be obtained in any other fashion. These surfaces may provide novel templates for overlayer growth and may serve as an important new starting point for surface oxidation.

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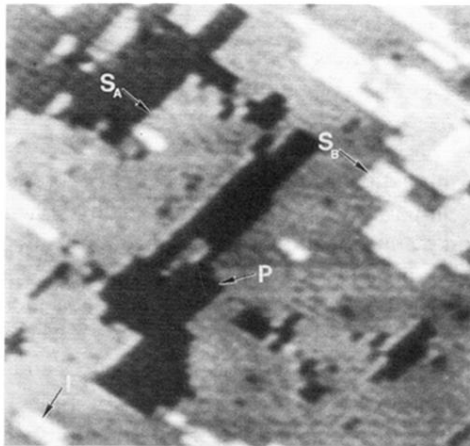


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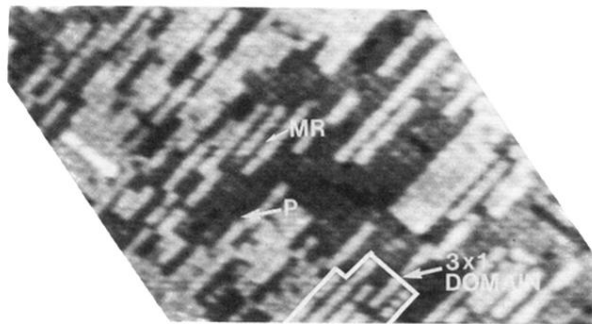


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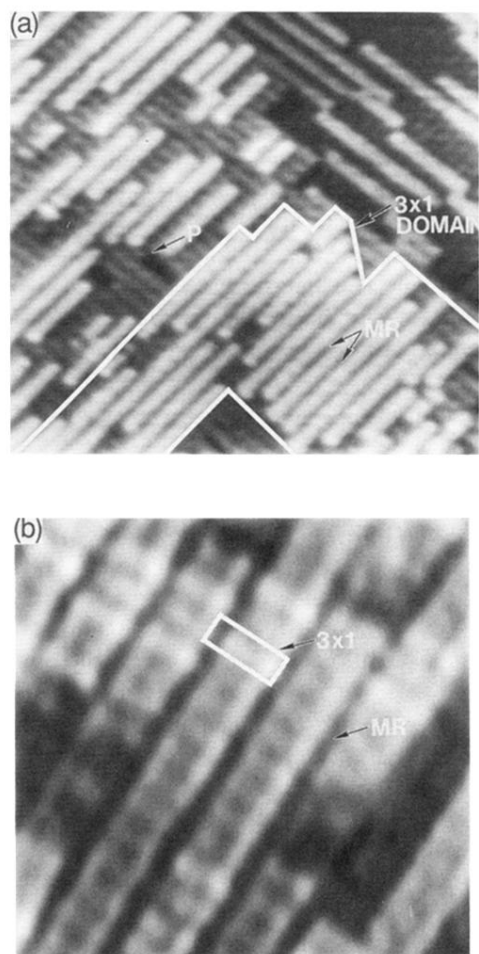


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