Selective Photobleaching of (−Ag−O−) Strings on the Ag(110) Surface

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Abstract: A p(2×3)-N Ag(110) surface obtained by N^+ and/or N_2^+ ion bombardment gave a desorption peak of N_2 at 530 K. When this p(2×3)-N Ag(110) surface was exposed to O_2 at room temperature, the LEED pattern showed a combined structure of [p(2×3)-N + p(2×1)-O]. The STM image proved the growth of the (−Ag−O−) and (Ag_2N) strings in the [001] and [1$\bar{1}$0] directions, respectively. The TPD spectrum of the combined surface gave the desorption of N_2 at 530 K, NO at 490−520 K, and O_2 at 600 K. When this [p(2×3)-N + p(2×1)-O] Ag(110) surface was illuminated with a UV light at room temperature, the (−Ag−O−) strings in the STM image were selectively erased although the (Ag_2N) underwent little influence, and the LEED pattern changed to the p(2×3)-N structure. The TPD spectrum of the surface after the illumination gave only N_2. These results indicate that surface migration of N atoms triggers the reaction between N and N yielding N_2 as well as N and O yielding NO on the surface. Selective photobleaching for the combined structure may suggest a feasibility of atomic scale lithography of the surface by using photochemical reactions.

Introduction

So far the surface phenomena caused by interactions with gases have been explained by the adsorption of molecules or the atoms, but the formation of quasicompounds or pseudomolecules has been pointed out on metal surfaces by using scanning tunneling microscope (STM) studies.[1] Based on this idea, the p(*n*×1), p(2×1), and p(3×1) or p(2×1) structures appearing on Ag(110), Cu(110), and Ni(110) surfaces exposed to O_2 are explained by the growth of one-dimensional metal−oxygen strings in the [001] direction and their self-assembly, respectively. The growth of (−Cu−O−) chains on the Cu(110) surface is a kind of chemical reaction, and an intermediate of (CuO)* species is a precursor for the formation of a quasicompound of (−Cu−O−) chains as illustrated in Figure 1. Similar precursor species were also presumed to explain the temperature-dependent elastic reflection of electrons on a O_2 preadsorbed Ag(110) surface[2], and more direct evidence has been shown by the transportation of (CuO)* precursor from a Cu-coated W-tip onto the Ag(110) surface in the presence of O_2.[3] Based on this idea, we intended to grow the (−Cu−O−) strings on the Ag(110) surface by supplying (CuO)* intermediates on the Ag(110) surface and the growth of (−Cu−O−) chains in the [1$\bar{1}$0] direction on the Ag(110) surface was attained.[14] The (−Cu−O−) chains grown on the Ag(110) surface are less stable compared to those on the Cu(110) surface so that they undergo decomposition into uniform size $(Cu)_6$ cluster dots arrayed along the [1$\bar{1}$0] axis on the Ag(110) surface.[4]

In this paper, a combined structure of quasicompounds of (Ag_2N) and (−Ag−O−) strings was prepared on the Ag(110) surface. This new Ag(110) surface shows an interesting selective photobleaching of the (−Ag−O−) strings by a UV light and a simultaneous thermal recombination of N + N → N_2 and N + O → NO at the same temperature.

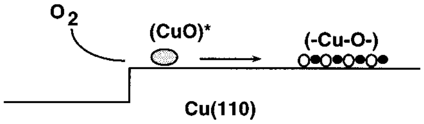

Figure 1. Growing of (−Cu−O−) strings via (CuO)* intermediates on the Cu(110) surface.

Experimental Section

The Ag(110) disk (10 × 13 × 1.5 mm^3) was cleaned by repeating Ar^+ ion sputtering and annealing at 620 K. The carbonaceous contaminants were removed by exposure to 1 × 10^{-4} Torr of O_2 for 10 s at room temperature and was followed by heating up to 670 K for 5 min. The temperature programmed desorption (TPD) experiments were carried out in a main UHV chamber and the illumination of the Ag(110) surface was performed by a high-pressure mercury lamp (500 W) through a sapphire window. The wavelength of the UV light was 310−510 nm. The scanning tunneling microscopy (STM) experiment was performed in another UHV chamber by using a Rasterscope-3000 (DME Co.). N atoms were supplied on the Ag(110) surface by N-ion bombardment (∼350 eV) at room temperature. The STM images were obtained by constant-current mode at room temperature with a W-tip.

Results and Discussion

The silver surface is inactive for the adsorption of N_2, but when a clean (1×1) Ag(110) surface was bombarded with N^+ and/or N_2^+ ions at room temperature, the LEED pattern changed to a p(2×3) pattern. Figure 2a is an STM image for the N-adsorbed Ag(110) surface, where many stripes are arranged in the three-lattice spacing toward the [001] direction, and Figure 2b shows the internal structure of the stripe having two times periodicity along the [1$\bar{1}$0] direction. These STM images of the p(2×3) structure are similar to that of the p(2×3)-N on the Cu(110) surface[5] and on the Ni(110) surface[6]. This stripe should

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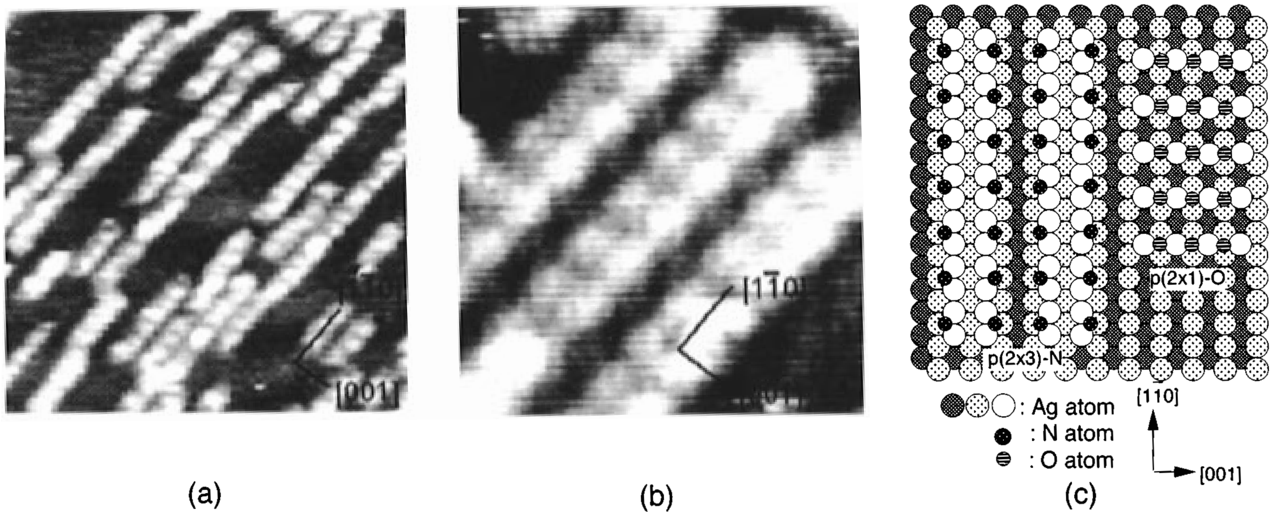

Figure 2. (a) STM image of the p(2×3)-N Ag(110) surface (175 × 175 Å^2) obtained by N-ion bombardment at room temperature. (b) Zoom-in image of the p(2×3)-N Ag(110) surface (44 × 44 Å^2). (c) The structural models for p(2×3)-N and p(2×1)-O on Ag(110).

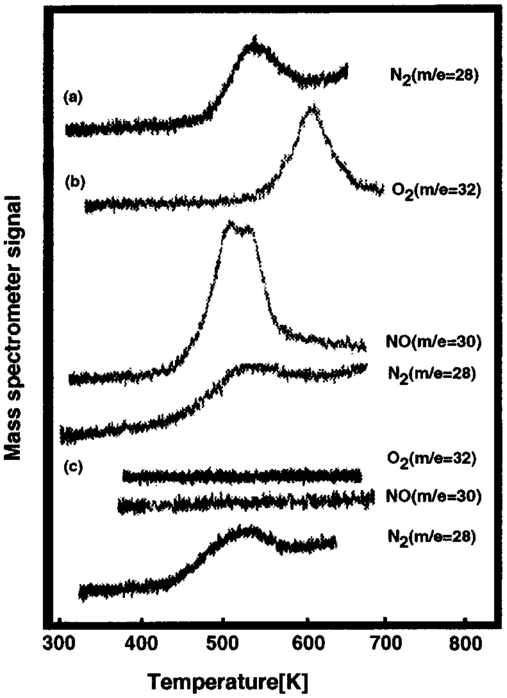

Figure 3. TPD spectra of N$_2$, O$_2$, and NO molecules desorbed from the Ag(110) surface. The heating rate was 3 K/s. (a) TPD spectrum of N$_2$ (*m/e* 28) from the p(2×3)-N Ag(110) surface. (b) TPD spectra of N$_2$ (*m/e* 28), O$_2$ (*m/e* 32), and NO (*m/e* 30) desorbing from the [p(2×1)(−Ag−O−) + p(2×3)(Ag$_2$N)] Ag(110) surface. (c) TPD spectra from the [p(2×1)(−Ag−O−) + p(2×3)(Ag$_2$N)] Ag(110) surface after UV illumination.

be assigned to the (Ag$_2$N) added row, a kind of quasicompound formed on the Ag(110) surface by reacting Ag atoms with N atoms. Figure 2c shows the model for the p(2×3)-N structure, details of which will be discussed elsewhere.[7] The desorption peak of N$_2$ (m/e=28) from the p(2×3)-N Ag(110) surface was observed at ca. 520 K as shown in Figure 3a and the p(2×3) LEED pattern disappeared. The STM image proved complete decomposition of the (Ag$_2$N) quasicompound.

When a p(2×3)-N Ag(110) surface such as shown in Figure 1a was exposed to 6000 L O$_2$ at room temperature, a combined LEED pattern for the p(2×1)-O + p(2×3)-N structures appeared. The STM image shows the growth of (−Ag−O−) strings in the [001] direction. The growth of (−Ag−O−) strings promotes arraying of (Ag$_2$N) sticks in p(2×3) as shown in Figure 4a. The model for [p(2×1)-O + p(2×3)-N] coexisting at the Ag(110) surface is shown in Figure 2c. The (−Ag−O−) strings on the clean Ag(110) surface prefer to disperse at low coverage by repulsive interaction,[8] but the (−Ag−O−) strings coexisting with (Ag$_2$N) stripes on Ag(110) are compressed by the growth of (Ag$_2$N) stripes. Similar compression of the (*n*×1) (−Ag−O−) strings was observed when CO$_2$ was adsorbed on the surface, where the carbonate species formed along the [001] direction compress the p(*n*×1) (−Ag−O−) structure into the p(2×1) structure.[9] The p(3×1) (−Ni−O−) Ni(110) surface is also compressed into the (2×1) arrangement by the growth of (−Ni−H−) strings in the [1$\bar{1}$0] direction[10] as well as by the adsorption of benzene[11] or NH$_3$.[12]

When a [p(2×1)-O + p(2×3)-N] Ag(110) surface was heated, not only the desorption of N$_2$ (490−520 K) and O$_2$ (600 K) but also the desorption of NO (m/e = 30) was observed at temperature very close to the N$_2$ desorption temperature as shown in Figure 3b. The NO molecule did not adsorb on the clean Ag(110) surface after exposure to 6000 L of NO, although a reference reported the desorption of NO from the Ag(110) surface at 390 K.[13] Therefore, the desorption of NO from the [p(2×1)-O + p(2×3)-N] Ag(110) surface is responsible for the reaction of N and O. Although NO does not adsorb on the clean Ag(110) surface, the sticking probability of NO on the p(2×1)-O Ag(110) surface was found to be rather high, but the desorption occurs at about 480 K, which is apparently lower than the desorption peak of NO from the [p(2×1)-O + p(2×3)-N] Ag(110) surface shown in Figure 3b. By adsorbing ^{15}NO on the [p(2×1)-O + p(2×3)-^{14}N] Ag(110) surface, it was confirmed that ^{15}NO was desorbed at around 480 K and ^{14}NO appeared at 520−530 K. These results evidently indicate that

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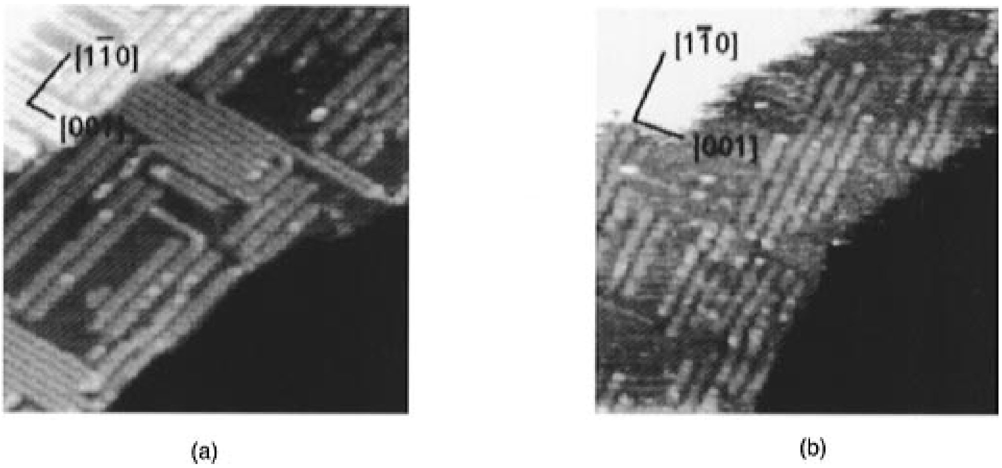

Figure 4. (a) STM image of a combined arrangement of the $p(2\times3)$ (Ag_2N) and the $p(2\times1)$ (−Ag−O−), which was prepared by exposing a $p(2\times3)$-N Ag(110) surface to 6000 L of O_2 at room temperature (241 × 241 $Å^2$). (b) Selective photobleaching of the (−Ag−O−) strings on a [$p(2\times3)$(Ag_2N) + $p(2\times1)$(−Ag−O−)] combined Ag(110) surface (288 × 288 $Å^2$).

^{14}NO molecules are directly produced by the reaction of ^{14}N with oxygen. Therefore, we can conclude that the mutual collision of N atoms yields N_2 and the collision of N atoms with (−Ag−O−) strings yields NO so that NO and N_2 molecules desorb at the same temperature as observed in Figure 3b.

When a $p(2\times1)$-O Ag(110) surface was illuminated with UV light for 15−30 min at room temperature, the LEED pattern underwent a sequential change from the (2×1) to (3×1), (4×1), and finally (1×1), showing no oxygen remained by the AES. On the other hand, when a [$p(2\times1)$-O + $p(2\times3)$-N] Ag(110) surface was illuminated at room temperature, the (2×1) LEED spots were selectively erased while the $p(2\times3)$-N structure remained. This result indicates that the thermal effect from the illumination can be ignored in this decomposition of (−Ag−O−) strings because the (Ag_2N) is less stable than (−Ag−O−) strings on the Ag(110) surface. In fact, the substrate temperature was carefully kept less than 330 K during the illumination. Therefore, it can be concluded that a selective photodecomposition of (−Ag−O−) strings occurs on the Ag(110) surface. In addition, only N_2 desorption occurred but neither O_2 nor NO desorption peaks appeared in the TPD spectrum for [$p(2\times1)$-O + $p(2\times3)$-N] Ag(110) surfaces after the illumination as shown in Figure 3c. That is, the recombination of N atoms takes place but the reaction between N and (−Ag−O−) does not exist. Figure 4b is an STM image which proves a selective photobleaching of the (−Ag−O−) strings, where only the $p(2\times3)$ (Ag_2N) structure remained on the Ag(110) surface after the illumination. It should be pointed out that Figure 4a and 4b are not the images for the same area because the illumination was performed by taking the sample out of the STM holder, but the TPD results undoubtedly prove the selective photobleaching of the (−Ag−O−) strings.

It was observed by STM that when a $p(2\times1)$-O Ag(110) surface was exposed to 1×10^{-8} Torr of CO at room temperature, (−Ag−O−) strings reacted with CO to produce CO_2 with a decrease in the number of (−Ag−O−) strings. The unreacted (−Ag−O−) strings kept almost the same positions.[14] That is, they keep the $p(2\times1)$ arrangement. In fact, a $p(2\times1)$ LEED pattern remains during the CO reduction at room temperature although the coverage of oxygen is lowered.[15] This indicates less mobility of the (−Ag−O−) strings arranged in $p(2\times1)$ on the Ag(110) surface at room temperature. In fact, sequential change of the LEED pattern from $p(2\times1)$ to $p(3\times1)$, $p(4\times1)$, and finally $p(1\times1)$ was observed at temperatures higher than 390 K during the CO reduction.[15] Taking these facts into account, it is a noteworthy fact that although substrate temperature was lower than 330 K, the illumination underwent a sequential change of the $p(n\times1)$-O LEED pattern. We presumed that (−Ag−O−) strings are more mobile on the Ag(110) surface during the illumination. On the other hand, we have to keep in mind that the lifetime of an excited state is in general very short on the surface, that is, the excess energy given by the illumination would be rapidly quenched before the rearrangement of (−Ag−O−) strings in $p(n\times1)$. If this is the case, the apparent high mobility of (−Ag−O−) strings with illumination may be responsible for the formation of highly mobile (AgO)* intermediates. That is, the local Ag−O bond may be broken by the UV light and (AgO)* and O* intermediates are produced. These spices are highly mobile so that they undergo rearrangement in $p(n\times1)$ on the Ag(110) surface even at room temperature. The produced (AgO)* intermediate may contribute to the formation of O_2 and/or O* intermediates which are dissolved into the bulk. As a result, a sequential change of the $p(n\times1)$-O LEED pattern with decreasing oxygen coverage occurs on the Ag(110) surface with illumination. It should be pointed out that the O* atoms produced by the photodecomposition of (−Ag−O−) strings do not react with (Ag_2N) stripes although N atoms produced by the thermal decomposition of (Ag_2N) react with (−Ag−O−) strings to produce the NO molecule. This fact supports the idea that the (AgO)* and/or O* spices produced by the illumination may not have high excess energy due to rapid quenching. Details of the mechanism for the photodecomposition of the Ag−O bond are not clear at the present time because we used only a high-pressure mercury lamp (500 W) without a filter for this study.

It is an interesting subject to protect a part of the photosensitive phase from the illumination. We could say that the reaction of the $(n\times1)$ Ag(110)−O surface with CO_2 is a topographic masking reaction. Carbonate (CO_3) species are formed along the (−Ag−O−) strings in the [001] direction on the Ag(110) surface[9] according to the reaction $AgCO_3 \rightleftarrows (-Ag-O-) + CO_2$, and the carbonated part is insensitive to the photodecomposition. Therefore, the (−Ag−O−) strings can be recovered

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by heating after the illumination. In the case of carbonates on the Ag(110) surface, the p(2×1) pattern of (−Ag−O−) strings can not be recovered because the carbonate species are spread over the terrace when the (−Ag−O−) strings are bleached by illumination. However, selective photobleaching for the combined structure may suggest a feasibility of atomic scale lithography of the surface by using photochemical reactions.

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