Determination of silver coverage on Si(111) 3×1(6×1)-Ag surfaces

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The number of silver atoms incorporated into a Si(111) 3×1(6×1)-Ag structure is determined by scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES). Silver MNN Auger intensities from surfaces with two different compositions were compared between clean 7×7, $(\sqrt{3}\times\sqrt{3})R\,30°$-Ag, and 3×1(6×1)-Ag structures, which were determined from scanning tunneling microscopy images. From the AES intensity ratio and known occupancies of each reconstruction, the number of Ag atoms incorporated into the 3×1(6×1)-Ag structure was determined to be 0.36 ± 0.16 ML. This value is close to $\frac{1}{3}$ ML, suggesting that one of the two rows observed by STM does not consist of Ag atoms.

Determining the number of atoms in a surface reconstruction is the first step in investigating the atomic structure of the reconstruction. As a prototypical metal-induced reconstruction, Ag adsorption on silicon surfaces has been thoroughly investigated. It is now well established that two distinctive reconstructions are formed on a Si(111) surface depending on the Ag coverage and the temperature.[1] One has a $(\sqrt{3}\times\sqrt{3})R\,30°$ unit cell and 1 ML $(=7.83\times10^{14}/cm^2)$ of Ag forms honeycomb structure ($\sqrt{3}$-Ag for short) around Si trimers. The whole atomic geometry was recently determined by Takahashi et al.[2] and is called the honeycomb-chain-triangle structure. The other structure has a 3×1 unit cell (3×1-Ag for short) and it converts to 6×1 below 200 °C.[1] Ag coverage of the 3×1-Ag reconstruction was thought to be $\frac{1}{3}$ ML,[3] however, further studies by Auger electron spectroscopy[4] (AES) and ion scattering spectroscopy[5] show different coverages and no consensus has been reached. Moreover, Fan and Ignatiev measured the Ag coverage in 3×1-Ag by Auger electron spectroscopy (AES) and found that the amount of Ag was well below $\frac{1}{3}$ ML.[6] They concluded that there is no long-range order of Ag atoms in the 3×1-Ag structure. However, this conclusion seems to be incompatible with the results of several atom-selective studies and with recent scanning tunneling microscopy (STM) observations.[7,8] In particular, Lin, Wan, and Nogami performed a comprehensive study on Ag adsorption on Si(111) surfaces[8] and observed that two clear stripes run along the 1× directions ($\langle 1\bar{1}0\rangle$ directions). This suggests that two rows are regularly occupied by some atoms. They proposed a structural model based on their STM observation. In their model, π bonded chains of Si atoms along the $\langle 1\bar{1}0\rangle$ direction were formed on bulk terminated Si(111), and Ag atoms were bonded to each dangling bond of Si atom, resulting in $\frac{2}{3}$ ML of Ag being incorporated into the 3×1-Ag reconstruction. However, this model seems to contradict several early investigations and the fact that the 3×1 surface has semiconducting surface electronic states, because one dangling bond remains in their model. It is not probable that the dangling bond is completely occupied or unoccupied by the charge transfer of surrounding atoms.

This confusion may arise from determining the coverage without knowledge of the spatial distribution in the 3×1-Ag reconstruction. Usually, when we determine the surface coverage, we assume a priori a uniform surface, that is, the entire surface is covered with one kind of reconstruction. This is true in most cases, however, a recent low-energy electron microscopy study[9] and STM study[8] showed that a uniform 3×1-Ag surface cannot be formed, but instead, is always accompanied by a 7×7 clean surface and/or a $\sqrt{3}$-Ag surface. Therefore, knowledge of spatial distribution in 3×1-Ag reconstructions is essential in determining the surface Ag coverage. In this paper the surface coverage of Ag atoms in 3×1-Ag surfaces was studied by AES and STM. AES intensities were calibrated by a known surface occupancy of the $\sqrt{3}$-Ag reconstruction, assuming a Ag coverage of 1 ML.

Experiments were performed to confirm this. First, $\sqrt{3}$-Ag surfaces were formed by depositing of about 0.5 ML of Ag on thermally cleaned n-doped Si(111) surfaces at room temperature and then annealing them at 540 °C for 10 min. A $(\sqrt{3}\times\sqrt{3})R\,30°$ structure was confirmed by low-energy electron diffraction and STM. The ratio between the $\sqrt{3}$-Ag and clean 7×7 regions were measured by STM and this surface is used as a reference for the Ag $M_{4,5}N_{4,5}N_{4,5}$ Auger signal (356 eV) intensity. Next, the surface was annealed again at 610–620 °C for 10 min to form a 3×1-Ag and $\sqrt{3}$-Ag mixture. The occupancies between the clean 7×7, 3×1-Ag, and $\sqrt{3}$-Ag regions were again measured by STM and the average Ag coverage was measured by AES. The coverage of Ag atoms in the 3×1-Ag can be determined from a known decrease in the AES intensity when annealed at 610–620 °C and by the known conversion areas from $\sqrt{3}$-Ag to 3×1-Ag.

The experiments were carried out in ultrahigh-vacuum (UHV) chambers equipped with a scanning tunneling microscope, an electron gun, and a hemispherical electron analyzer for Auger spectroscopy. Ag was deposited in a separate chamber attached to the STM-AES chamber. The samples were heated by combining the direct current heating to clean the sample and radiative heating from the backside of the sample to anneal it to make the sam-

ple temperature uniform. The sample temperatures were measured with an optical pyrometer. The pressures for Ag deposition, STM observation, and AES measurement were 2×10^{-8}, 1×10^{-8}, and 5×10^{-8} Pa, respectively. STM topographies were acquired at room temperature with a sample bias of 2.0–2.4 V and tunneling current of 0.5 nA. For six to eight 100 nm $\times$ 100 nm areas, within 2 μm $\times$ 2 μm were randomly chosen to evaluate the surface occupancy of each reconstruction. Ag MNN AES differential spectra were recorded with a 2-kV electron beam with a 1.5-μA sample current. Typically, the ener-

gy range of 25 eV is scanned in a minute and the signals of three different positions are averaged. The stability of the intensity of the Ag MNN spectra was $\sim 5\%$ within several hours.

Typical examples of STM images after annealing at 540 °C and annealing at 615 °C are shown in Figs. 1(a) and 1(b), respectively. Since the height between the 7×7 region and the $\sqrt{3}$-Ag region is different by 0.2 nm, differential height images are presented for clarity. In Fig. 1(a), it is difficult to resolve the $\sqrt{3}$-Ag reconstruction in this scale, however, the $\sqrt{3}$-Ag areas can be easily

(a)

(b)

(c)
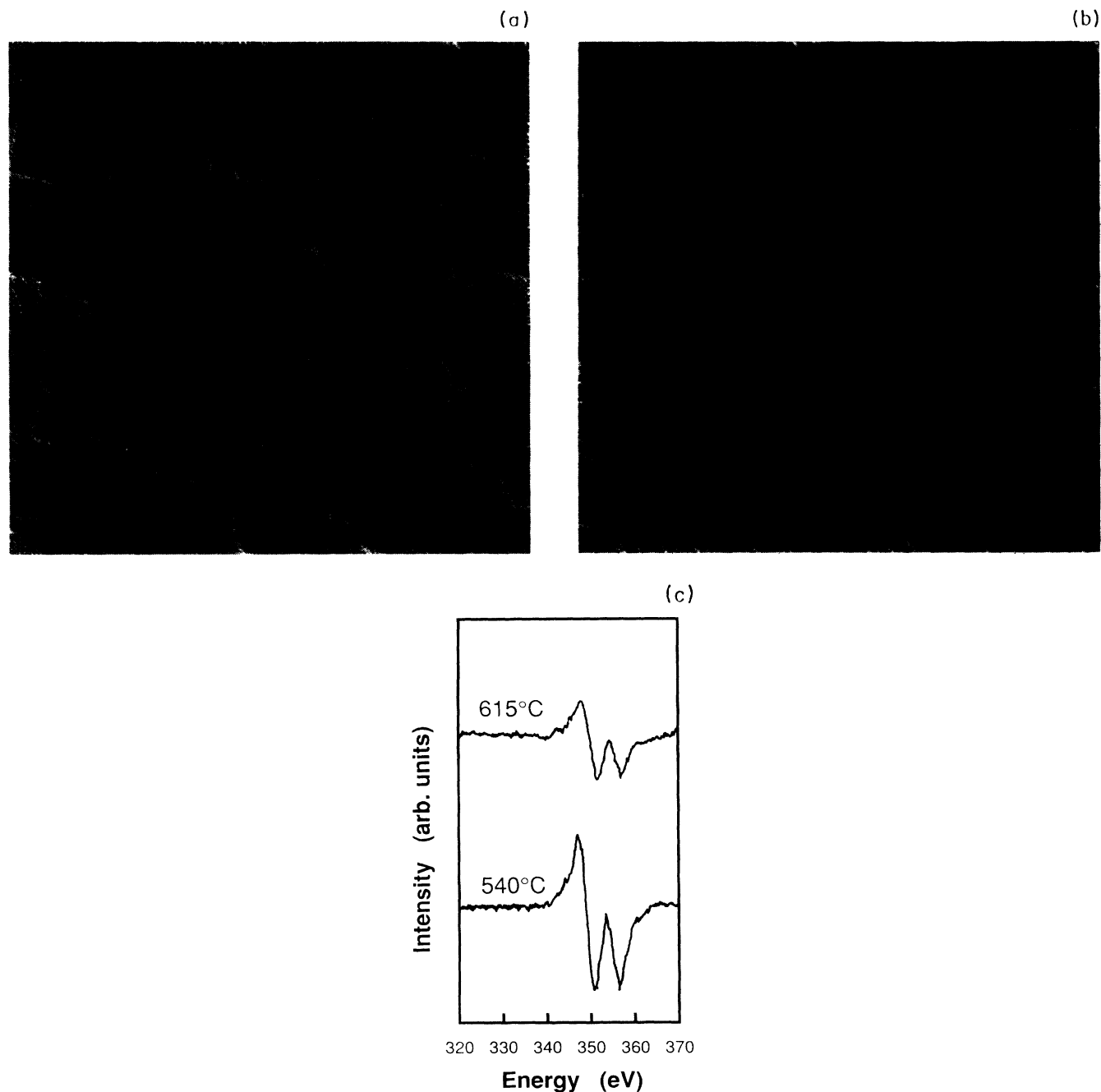

FIG. 1. STM differential images of the sample annealed at 540 °C (a) and 615 °C (b). The scanning areas are 100 nm $\times$ 100 nm. Silver MNN AES spectra (c) correspond to these surfaces.

TABLE I. Surface occupancies of the $\sqrt{3}$-Ag and 3×1-Ag areas before and after final annealing AES intensity ratios corresponding to before and after annealing are also tabulated.

| Sample number | Final annealing temperatures (°C) | Surface occupancies | | | AES ratio |
		Initial $\sqrt{3}$-Ag x_0	Final $\sqrt{3}$-Ag x	Final 3×1-Ag y	γ
1	610	0.58±0.06	0.28±0.05	0.22±0.05	0.67
2	615	0.45±0.05	0.09±0.04	0.47±0.09	0.50
3	615	0.39±0.06	0.01±0.01	0.33±0.06	0.27
4	620	0.50±0.06	0.004±0.01	0.41±0.06	0.28

separated from the 7×7 surface. Since the Ag is deposited at room temperature and the surface is annealed at a fairly low temperature, no preferential nucleation of the $\sqrt{3}$-Ag domain at the steps was observed. Small 3×1-Ag areas were found even at this temperature at the boundary between the $\sqrt{3}$-Ag and 7×7 areas or at the domain boundary of the $\sqrt{3}$-Ag structure. However, the occupancy of the 3×1-Ag is always less than 1% of the surface; therefore, it is neglected at this temperature.

The subsequent annealing results in conversion to the 3×1-Ag reconstruction [Fig. 1(b)], easily identified as lines along the $\langle1\bar{1}0\rangle$ directions. Almost all the $\sqrt{3}$-Ag reconstruction areas were converted to 3×1 at this temperature, but minor $\sqrt{3}$-Ag areas are still found in the upper right corner and lower left region of the image. Although the observed phase at this temperature is 3×1-Ag,[1,8] this observation seems not to conflict with the known phase diagram because the conversion from $\sqrt{3}$-Ag to 3×1-Ag takes a long time.[10] The domain size of each reconstruction was larger than that of the $\sqrt{3}$-Ag surface due to the diffusion of Ag atoms. Since each domain tends to be elongated in the $1x$ directions, the surface diffusion of Ag atoms may be quite anisotropic. Irregular parts are occasionally found on the surface, possibly due to the contamination resulting from the electron beam used in AES. Since the metallic 7×7 reconstruction may be more reactive than the semiconducting $\sqrt{3}$-Ag or 3×1-Ag areas, it is assumed that no Ag was adsorbed on these irregular parts.

Corresponding AES spectra are shown in Fig. 1(c). No notable differences in the spectrum shape were found between the surfaces annealed at 550 and 615°C except for the tails at the higher-energy side of the spectra. The relative magnitudes between the $M_{4,5}N_{4,5}N_{4,5}$ doublet were within 10% and their energies were within 0.5 eV in all measured spectra. This suggests that the chemical environment of Ag atoms is similar between the $\sqrt{3}$-Ag and 3×1-Ag structures. The Si LMM peaks also showed no differences among the 7×7 clean surface, $\sqrt{3}$-Ag, and 3×1-Ag reconstructions, suggesting again that the charge transfer from Ag to Si is not large.

To determine the Ag coverage in the 3×1-Ag reconstruction, four samples were analyzed. The surface occupancies of each structure and the AES intensity ratio of the samples annealed at 540°C and the final annealing temperatures are summarized in Table I. Statistical errors due to fluctuations in the occupancy measurement are also indicated. Typical statistical errors for determining the $\sqrt{3}$-Ag and 3×1-Ag areas are ~10 and $\sim20\%$

of the occupancies, respectively. These errors are understood from the fact that typical domain sizes of the reconstruction areas are roughly $300-600$ nm^2 and the total sampling areas are $6-8\times10^4$ nm^2. From these values, the Ag coverage of the 3×1-Ag structure (I) can be derived from the measured AES intensity ratio (γ),

$$I = \frac{\gamma x_0 - x}{y},$$

where x_0 and x are the surface occupancies of a $\sqrt{3}$-Ag surface before and after final annealing, respectively, and y is the surface occupancy of 3×1-Ag after final annealing. The result of Ag coverage on a 3×1-Ag surface is shown in Fig. 2 as a function of the final annealing temperature. The fluctuations in occupancy in the STM images are indicated as error bars in the figure. Since the 3×1-Ag conversion area was small when the sample was annealed at 610°C, the error is fairly large for sample 1. All data points go across the $\frac{1}{3}$ ML line indicated by a heavy broken line in the figure. By averaging these four data the Ag coverage on the 3×1-Ag structure is determined to be 0.36 ± 0.16 ML, which is in close agreement with $\frac{1}{3}$ ML. This strongly indicates that one Ag atom is incorporated into the 3×1-Ag reconstruction.

The model involving no ordering Ag atoms[6] is apparently inconsistent with these results. In particular, although almost all of the surface annealed at 620°C was converted to 3×1-Ag structure, AES intensity is still
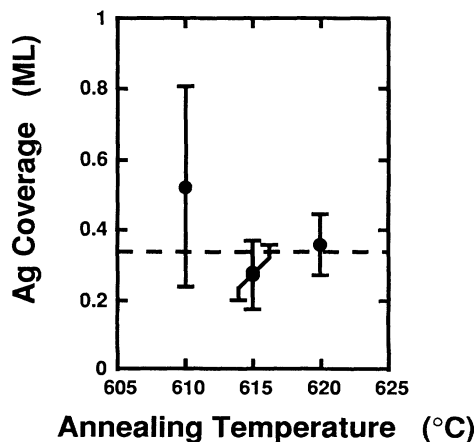

FIG. 2. Ag coverage determined from Table I as a function of the final annealing temperature. $\frac{1}{3}$ ML is indicated by a broken line.

only about $\frac{1}{3}$ that of the $\sqrt{3}$-Ag surface (sample 4). The $\frac{2}{3}$ ML model based on STM observation,[8] is also incompatible with the present results. STM observation showed two distinctive protrusions in a unit cell in the empty state image, one of which is higher than the other.[8] One possible explanation for this is that one of the rows is occupied by Ag atoms and the other row by Si atoms. Since the ion scattering experiment[4,5] showed that Ag peaks still appeared at a lower angle in this structure than in the $\sqrt{3}$-Ag surface, the higher row may consist of Ag atoms. From the reported number of Si atoms incorporated into the 3×1-Ag structure[11] and the $\frac{1}{3}$ ML of Ag atom determined in the present study, it is difficult to construct a specific model which is consistent with STM observations.

In conclusion, surface Ag coverage in the 3×1-Ag structure has been examined by combining AES and STM. The results show that Ag coverage on the 3×1-Ag structure is 0.36 ± 0.16 ML, which is in close agreement with the $\frac{1}{3}$ ML model. Therefore, only one of the two rows observed by STM consists of Ag atoms.

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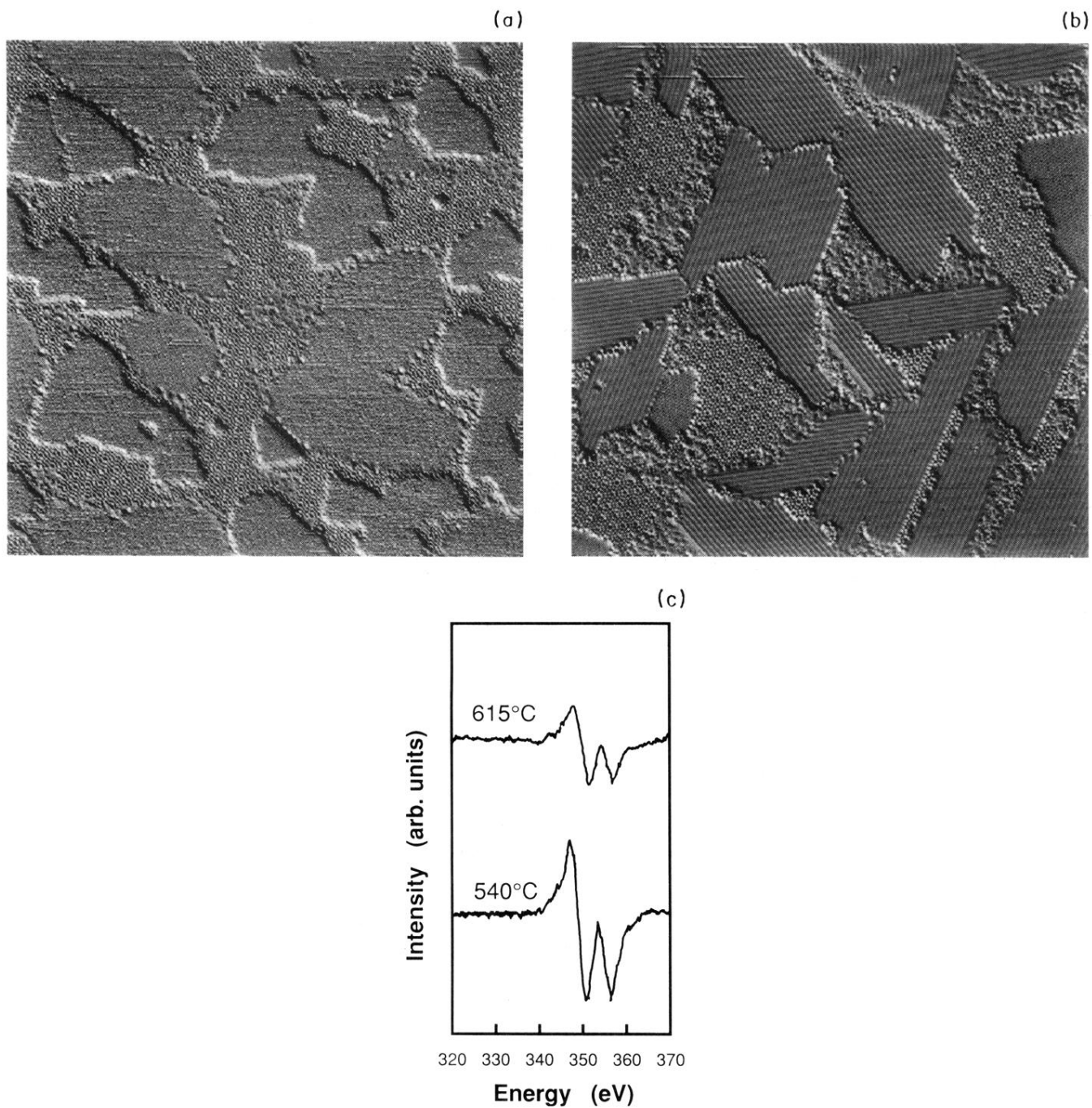
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