Structure of segregated Au layers on Ni(110)–0.8 at. % Au alloy by scanning tunneling microscopy

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The structure of segregated Au layers on the Ni(110)–0.8 at. % Au surface has been studied by scanning tunneling microscopy. The observed structures, including (7×4) with a $c(2\times4)$ subunit, are shown to be consistent with the observed low-energy electron diffraction pattern. Two different kinds of Au structures, commensurate atomic chains and incommensurate closed-packed atomic rows, were observed. A model for the nucleation and growth of the segregated layer is proposed.

Surface segregation, the enrichment of one component of some alloys on the surface of the solid, is of considerable scientific and technological interest as a way to prepare new surfaces.[1–3] Various alloy surfaces have previously been studied experimentally[2,4] and theoretically[2,5] to obtain the composition of the surface. While the importance of segregated surfaces has long been recognized, few investigations have been made of their equilibrium structures. Low-energy electron diffraction[6] (LEED) and low-energy ion scattering[7,8] (LEIS) have been used to determine structures, but these employ structural models fitted to either the diffraction patterns or the angular dependence of scattered ion intensities. In this paper we show the first direct image of a segregated layer, taken by scanning tunneling microscope (STM), with atomic resolution. We were able to resolve individual nearest-neighbor Au atoms with a lateral separation of 2.9 Å and a vertical corrugation of 0.2 Å between atoms. The structure obtained by STM can explain the complex observed LEED pattern and agrees with LEIS data in several essential details.

The segregation of Au in Ni-Au alloys[7,9,10] is expected on the basis of differences in atomic size and in the bond energies.[5] Previous LEED and LEIS studies[6,8] have identified a (7×7) reconstruction and have proposed an hexagonal Au surface structure, like the Au(111) surface, with $\langle 001\rangle$ antiphase boundaries and open channels along $\langle 1\bar{1}0\rangle$. In the present study, the surface periodicity identified by STM and LEED was (7×4), and some of the same features found in the previously proposed model were observed, including antiphase boundaries, facets, and channels. The dissimilarities between the present and previously observed structures on this surface may be due to different bulk compositions or different segregating conditions.

The design of the STM (Ref. 11) used in the present study has been described previously.[12] Briefly, an ultrahigh-vacuum chamber is equipped with STM, LEED, and Auger spectroscopy to study the sample surface and field-ion microscope (FIM) to characterize the STM tip. STM topographs were taken with a tip bias of -100 to -15 mV and a constant tunneling current of 0.5 to 1.0 nA. The Ni(110)–0.8 at. % Au single crystal was treated *in situ* by Ar sputtering and annealing below 600 K to create a clean, well-ordered (1×1) Ni(110) surface. Au was then segregated to the surface by annealing the sample between 900 and 1000 K. Coverage was controlled by varying the duration of the anneal, and was measured by the ratio between Ni and Au Auger peaks and by counting atoms in STM topographs. (The Auger peak ratio was previously calibrated by high-energy Rutherford ion backscattering.[10]) For most of the data presented here, the coverage of the Au layer is 0.9 ± 0.2 monolayers (ML).

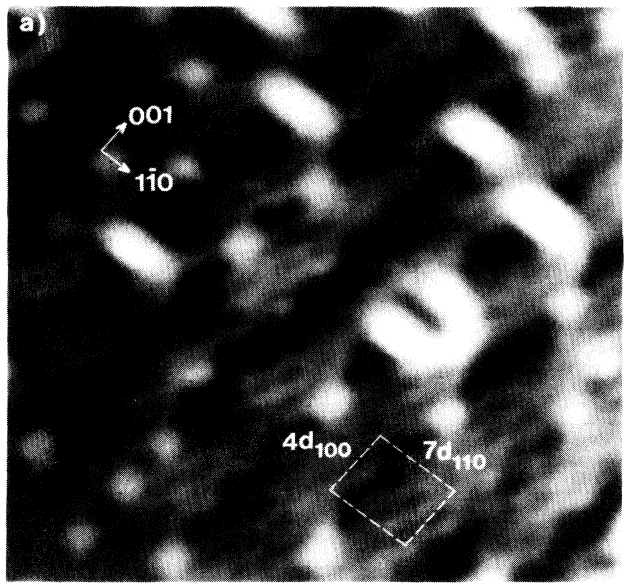
Figure 1(a) is a $(120\ \text{Å})^2$ STM topograph of the segregated Au layer, taken with a tip bias of -65 mV and a tunneling current of 0.5 nA. The total gray scale range from white (high) to black (low) is about 0.6 Å. The atoms appear to be arranged in chains grouped together to leave vacant channels of varying width along $\langle 001\rangle$. Bridges of atoms about 0.3 Å above the chains span the channels at many positions. Figure 1(b), a $(60\ \text{Å})^2$ topograph, shows the details of these features more clearly. The chains can now be seen as dimers along $\langle 001\rangle$, and the "bridges" are resolved into double rows of atoms along $\langle 1\bar{1}0\rangle$.

A schematic of the structure observed by STM is shown in Fig. 2(a). At left, Au-atom dimers in a $c(2\times4)$ arrangement are repeated at $7d_{110}$(Ni) and $4d_{001}$(Ni) intervals. This (7×4) unit mesh with a $c(2\times4)$ subunit is confirmed by the LEED pattern of the segregated layer shown in Fig. 2(b). In the $\langle 1\bar{1}0\rangle$ direction, two or three dimer chains form groups separated by open channels of width nd_{110} where n is odd, typically 1, 3, or 5. In many epitaxial systems, regularly spaced dislocations in the overlayer are produced by the lattice mismatch between the overlayer and substrate. In this case, since the long-range order appears to have a $7d_{110}$ spacing, the channels cannot be completely filled by the $2d_{110}$-wide $c(2\times4)$ subunits and thus act as antiphase boundaries. The small circles in Fig. 2(a) indicate second-layer Au atoms which are only occasionally observed by the STM, but there is substantial indirect evidence to support their existence. Low- and high-energy ion scattering studies, for example, have previously found shadowing of Ni atoms indicating that most of the hollow sites, energetically favorable positions, are occupied by Au atoms in the first and second layers.[8,10] This also justifies the proposed position of the Ni lattice atoms in Fig. 2(a) with respect to the observed Au atoms, although the Ni atoms are not directly observed by STM when Au is segregated. In addition, the

two-layer height of the present overlayer has been measured in STM topographs of surfaces with lower coverage of segregated Au.

The most unexpected features in Fig. 3 observed on the segregated surface were "bridges" (B) consisting of double rows of atoms in the $\langle 1\bar{1}0\rangle$ direction, spanning the open channels and connecting the atom chains. They began to appear when the coverage of the segregated layer exceeded about 0.7 ML. Details of these bridges are visible in a (60 Å)^2 topograph shown in Fig. 3(a). The bridge atoms were better imaged with the tip voltage between -35 and -15 mV, indicating that their local electronic structure differs from that of the chain atoms.[13,14] The structure of a bridge is schematically depicted in the upper part of Fig. 2(a). The number of atoms observed in the bridges varied from 8 to 14, two rows of seven atoms being most common. While the identity of the atoms is not revealed in a constant-current STM topograph, the distance (d_B) between bridge atoms was measured to be 2.9 Å, in close agreement with the Au$\langle 110\rangle$ nearest-neighbor distance, suggesting that they are indeed Au atoms. Atoms near the center of the bridge were found to be 0.4 Å higher than those at the ends. This is probably due to the mismatch of the Au lattice constant with that of the substrate, causing the bridge atoms to buckle slightly to different heights depending on their displacement from the registry position. One row of atoms in each bridge typically appeared to be slightly "higher" (≤ 0.1 Å) than the other row; this, of course, could represent a difference in electronic structure or an actual physical height change caused by local strain. The bridges appear to be distributed almost randomly, often associated with defects, and their density was dependent on the annealing history and the coverage of the sample. Figure 3(b) shows a facet of Au atoms. The oblong-shaped atomic rows are aligned along the $\langle 1\bar{1}0\rangle$ direction and are separated by 17.5 Å (d_0) in this direction, forming a (221) facet plane. Each row is 15.0 Å long, the same length as a bridge; in fact, the facets usually appeared to be nucleated from the bridge atoms (B).

Although the (7×4) usually appeared after our stan-



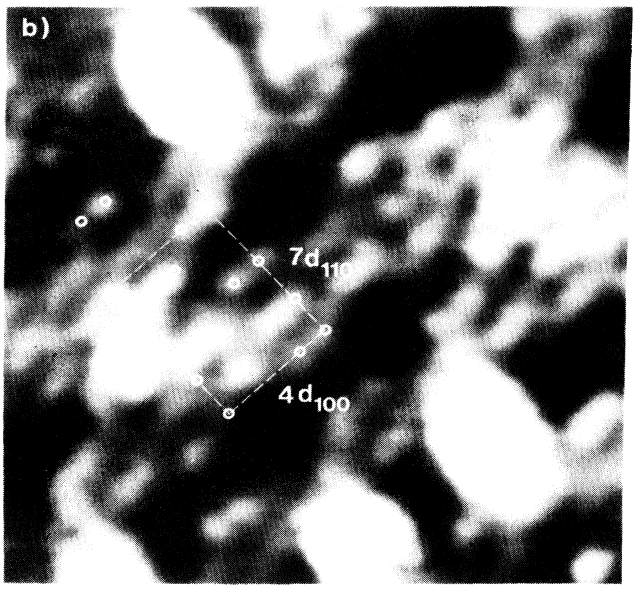


FIG. 1. (a) (120 Å)^2 gray-scale topograph of the Au segregated layer on the Ni(110) surface. A unit cell of the (7×4) reconstruction is shown. Most of the area is covered with the (7×4), while some local disorder. (b) (60 Å)^2 topograph of the Au segregated layer with $V_{tip} = -50$ mV. A (7×4) unit cell is a rectangle and a $c(2\times4)$ subunit (a diamond).

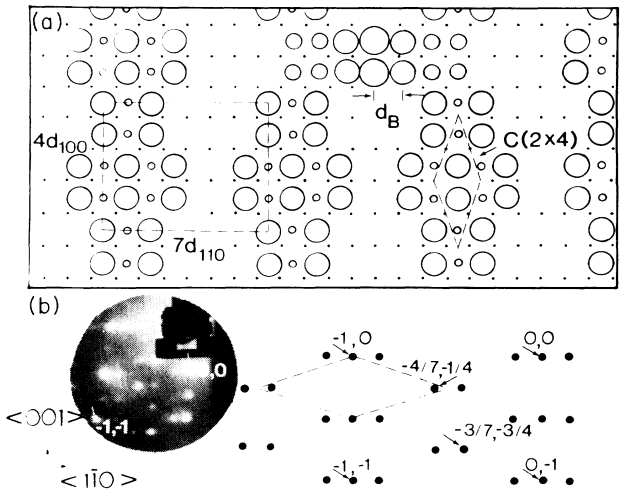


FIG. 2. (a) Schematic of surface structure observed by STM, showing (7×4) (rectangle) and a $c(2\times4)$ subunit (diamond). Structure of "bridge" atoms (upper part) is shown. Dots indicate Ni atom positions, and large and small circles indicate Au atoms in the first and second layer, respectively. (b) LEED pattern for (7×4) reconstruction. Spots are schematically shown at right. Enhancement of the spots near $c(2\times4)$ unit is shown by dashed line.

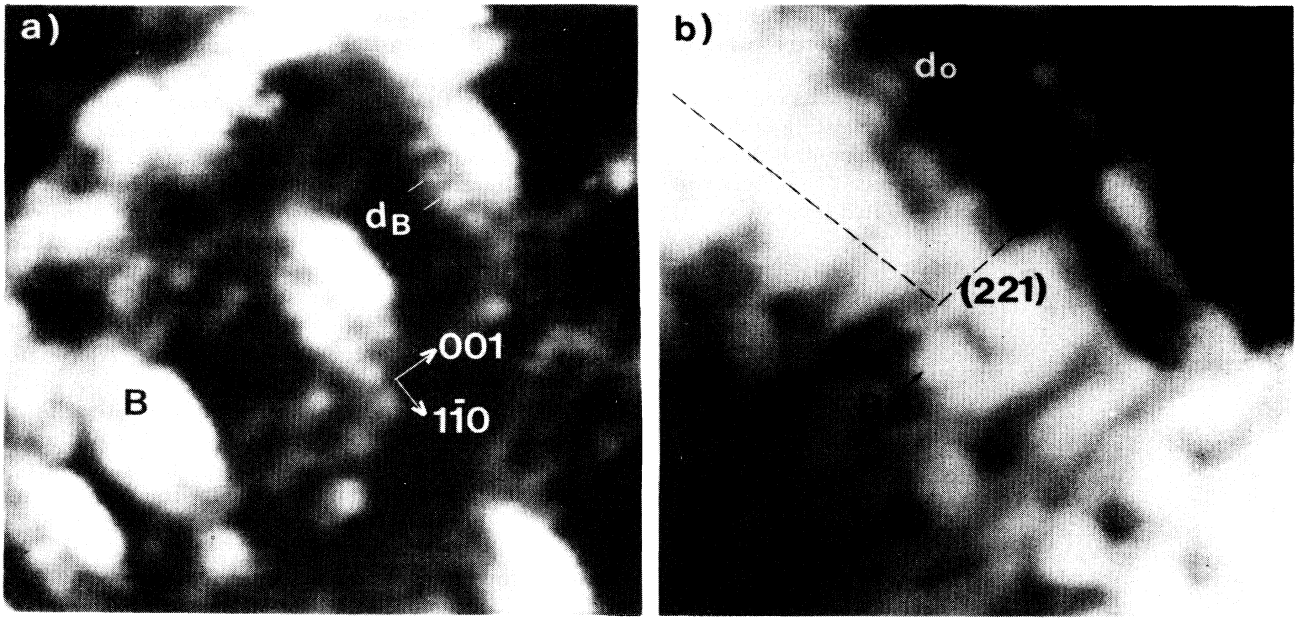


FIG. 3. (a) (60 Å)^2 topograph of the Au segregated layer with $V_{tip} = -35$ mV. Individual atoms in "bridges" are 2.9 Å apart along the $\langle 1\bar{1}0 \rangle$. Each bridge consists of two rows of seven atoms. (b) (120 Å)^2 topograph of the Au(221) facet, indicated by an arrow.

dard annealing conditions, areas showing other structures, including (7×2), (5×4), and (2×1), were sometimes found, possibly due to local differences in Au coverage. The observation of these minor domains suggests a growth mechanism of the segregated layer. On a surface with low Au coverage, a variety of chains were found along the $\langle 001 \rangle$ direction, including straight chains (2×1), monomer chains $[c(2\times2)]$ forming (7×2), and dimer chains $[c(2\times4)]$ forming (7×4). In all of these structures, the subunits are $2d_{110}$ (5.0 Å apart) wide along $\langle 1\bar{1}0 \rangle$, since Au atoms cannot occupy the adjacent commensurate positions of Ni (2.5 Å apart) due to the repulsive force between Au atoms, for which the nearest-neighbor separation is 2.9Å. As coverage increases, long-range order is formed with a periodicity of 7 along $\langle 1\bar{1}0 \rangle$ and of 4 along $\langle 001 \rangle$. The driving force for the long-range order may be the periodic potential produced by the large lattice mismatch (16%) between Au and Ni.[15]

The interaction between an overlayer and a substrate may change with the coverage of the overlayer. The change could also result in a transition of the growth mode. In this study, at coverages of less than 0.7 ML, only commensurate positions of Au atoms in the chain structures, determined by the Au—Ni bond, exist. At coverages greater than 0.7 ML, Au atoms appear at incommensurate sites in the bridges, separated by the bulk Au nearest-neighbor distance indicating stronger Au-Au bonding. The bridges are also believed to be seeds of the Au facets. The observed structure is evidently an example of Stranski-Krastanov growth;[16] once the overlayer reaches a certain coverage, its interaction with the substrate is reduced and the bulk like overlayer is formed. Studies at higher Au coverage, produced by deposition (since segregation seems to be self-limiting at ~ 1 ML), may further illuminate the growth mechanism.

The observed (7×4) structure is one of the most complex surfaces investigated by STM. As in previous studies, it has been demonstrated that a surface structure that would be difficult to unravel from LEED or ion scattering data alone can be directly revealed on an atomic scale using STM.

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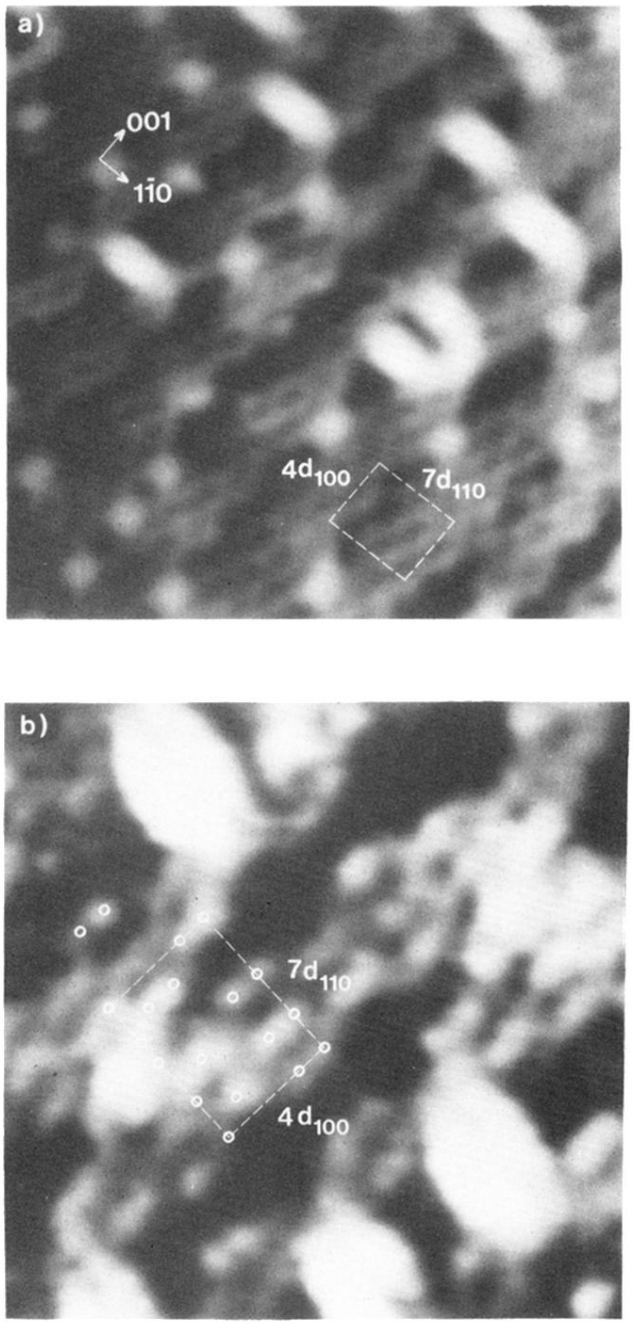

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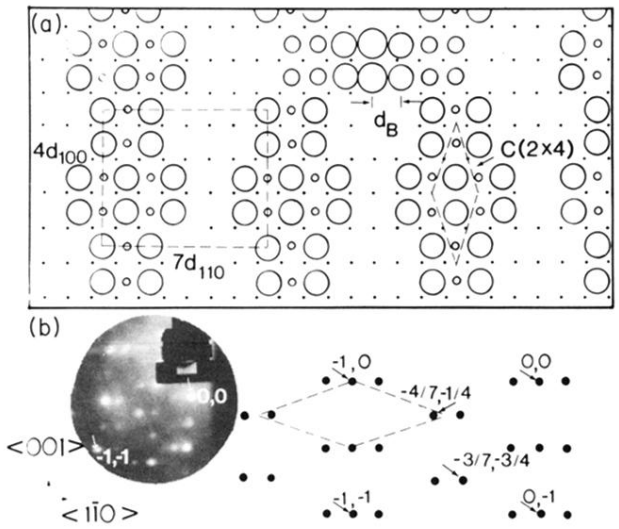

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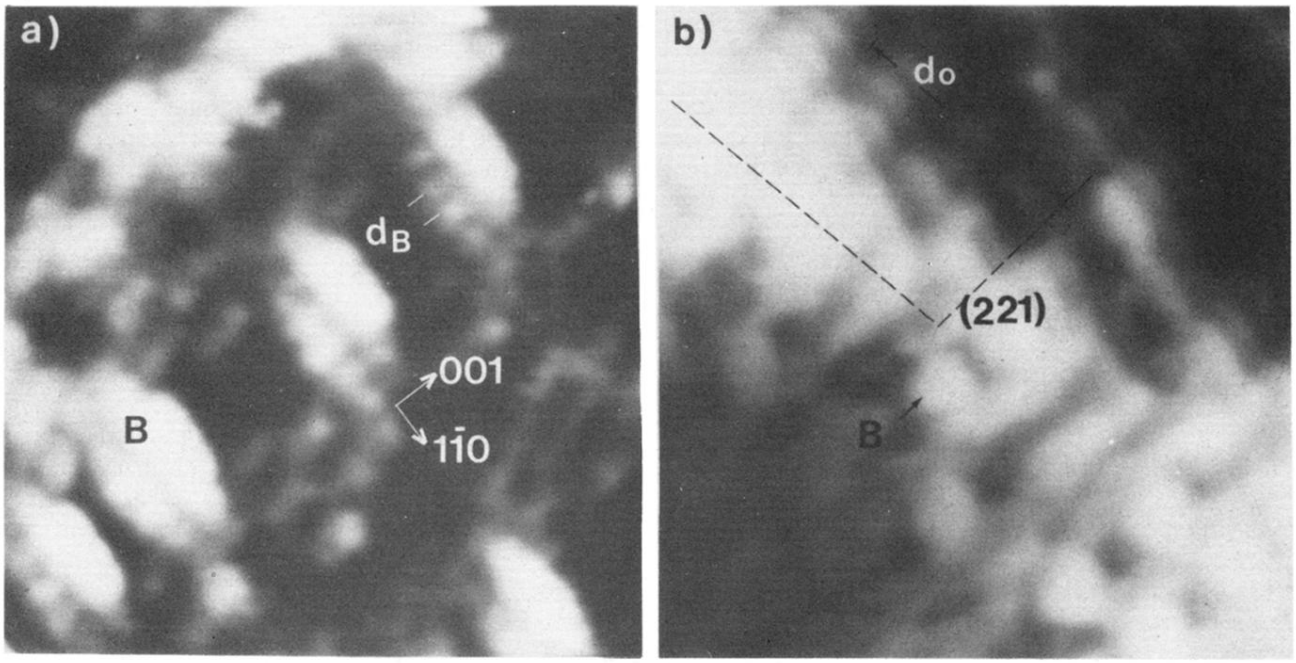

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