Surface Science 287/288 (1993) 941–945
North-Holland

surface science

Epitaxial growth of Au on Ag(110) studied by scanning tunneling microscopy

S. Rousset [1], S. Chiang, D.E. Fowler and D.D. Chambliss
IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099, USA

Received 31 August 1992; accepted for publication 24 November 1992

The epitaxial growth of Au on Ag(110) has been investigated by scanning tunneling microscopy up to 3 ML. A very consistent "intermixed Stranski–Krastanov" growth mode is demonstrated. Below 1 ML the open structure of the (110) surface allows the Au atoms to be incorporated mainly in the second layer. At higher coverages three-dimensional anisotropic islands of gold are observed. The anisotropic shape, the island density and the transition from two-dimensional to three-dimensional growth are discussed.

1. Introduction

Among the great variety and complexity of epitaxial growth [1,2] a few metal on metal systems have been recently investigated by scanning tunneling microscopy (STM). Ni deposited on Au(111) [3] at room temperature reveals ordered nucleation sites which are identified as surface-lattice dislocations. Fractal islands or fingers observed in different systems [4] are in agreement with a two-dimensional (2D) diffusion-limited-aggregation (DLA) growth model. Although such important features have been identified, they concern mainly the layer-by-layer growth mode on a densely-packed surface.

In this paper the deposition of gold on the open silver (110) surface has been studied up to 3 ML. The striking growth mode of this system is first investigated. Both STM images and previous medium energy ion scattering (MEIS) [5,6] data are necessary in drawing the conclusion of an "intermixed Stranski–Krastanov" (SK) growth mode. Then the density, shape and formation process of the three-dimensional (3D) islands are examined.

2. Experimental

These experiments were performed in a multiple-chamber ultrahigh vacuum STM apparatus described in detail elsewhere [7]. The Ag(110) crystal was cleaned by Ar-ion bombardment (500 eV) and flash annealed at 600°C. After the sample was allowed to cool for at least one hour to reach room temperature, it was exposed to Au flux evaporated from a tungsten basket. Absolute calibration of the Au coverage (θ) within 20% was ensured by the following procedure. A line-of-sight ionization gauge indicates a pressure proportional to the rate of evaporation. The flux was calibrated by optimizing the sharp c(2 × 2) low energy electron diffraction (LEED) pattern obtained when 0.5 ± 0.1 ML of Au is deposited onto Cu(100) [8]. Most of the evaporations were performed at a constant rate of 0.6 ML/min (1 ML Ag(110) = 8.45×10^{14} atoms/cm^2) with a constant pressure of 2.5×10^{-9} Torr read by the line-of-sight ionization gauge during the evaporation. Experiments were performed with different deposition rates, ranging from 0.4 to 2 ML/min,

[1] Permanent address: Groupe de Physique des Solides, CNRS–Université Paris VI et VII, Tour 23, 2 Place Jussieu, 75251 Paris Cedex 05, France

without any qualitative change in the results. Following sample preparation, no contamination of the surface with O or C was found by Auger spectroscopy, and the observed LEED pattern is (1×1) for all coverages. The STM images were acquired in a constant current mode, mainly with negative sample voltage from 30 mV to 2 V and tunneling current from 1 to 2 nA. Positive sample polarity did not show any spectroscopic effects.

3. Results

3.1. Growth mode

Since the lattice parameters of both metals ($a_{Au} = 4.08$ Å and $a_{Ag} = 4.09$ Å) and their surface free energy ($\gamma_{Au} = 1.6$ J/m^2 slightly larger than $\gamma_{Ag} = 1.3$ J/m^2) are very close, a layer-by-layer or Frank–van der Merwe (FM) growth mode is expected. Although this is observed for the deposition of Au on Ag(111) [9] and on Ag(100) [10], a recent study by MEIS [5,6] showed that the growth on the more open (110) surface is totally different: it has been interpreted as a bilayer growth mode which starts as soon as 0.06 ML of gold is deposited.

STM data (fig. 1a) show that below 1 ML no islands nucleate and that all of the steps, with or without gold, are monatomic steps, 1.45 Å high. Thus a bilayer growth does not occur. Only two growth modes are consistent with the STM data: either Au atoms sit on top of the Ag substrate, such as ideal FM or SK modes, or interfacial alloying has to be taken into account. For samples prepared under similar conditions, the MEIS data show a "blocking dip curve" (fig. 2 in ref. [5]), proving that the deposited Au atoms are shadowed for $\theta \geq 0.06$ ML. This result rules out an ideal FM or SK mode and shows that alloying must take place. Therefore we have reinterpreted the MEIS blocking curve, allowing for three locations of gold atoms: regions of Au monolayer on top of the Ag(110) surface, regions of Au incorporation below the top layer of the Ag(110) surface and Au bilayers. Standard Monte Carlo type scattering calculations [11] were used to determine the fractions of the surface covered by each

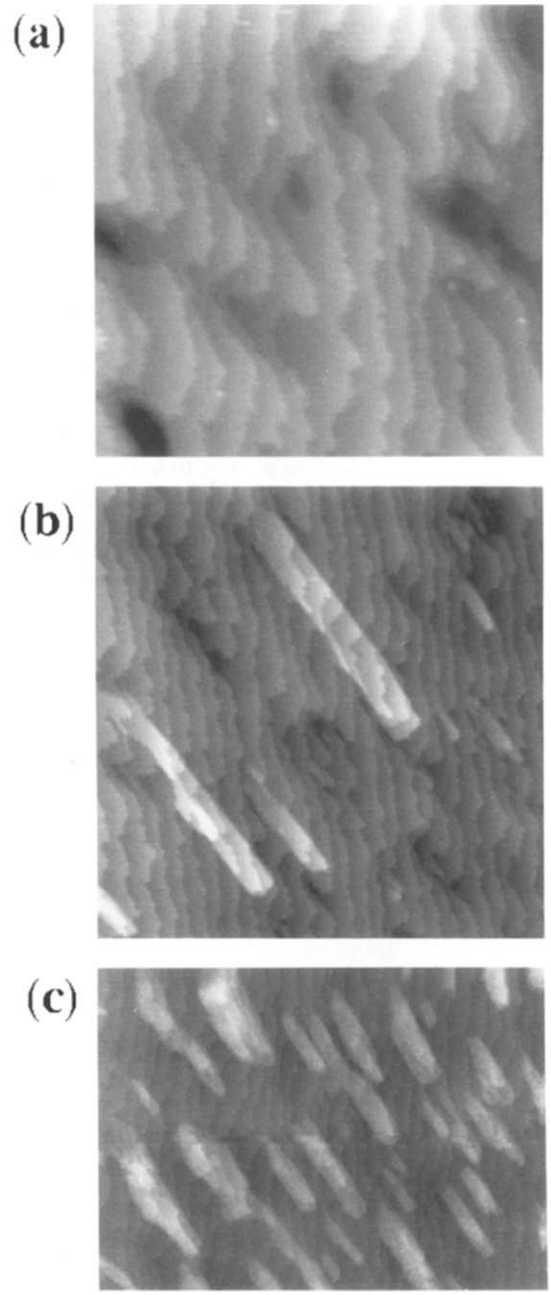

Fig. 1. STM top view images for different Au coverage (θ) on Ag(110): (a) 900 Å×900 Å image for $\theta = 1$ ML, (b) 1500 Å×1500 Å image for $\theta = 1.4$ ML, (c) 3000 Å×3000 Å image for $\theta = 3$ ML.

of these three possible Au/Ag configurations. The details of the simulation are given elsewhere [12]. The results of our modelling give a best fit to

the blocking curve data when nearly all of the Au atoms are located below the top Ag layer. Thus, for submonolayer coverage of Au, the combination of STM and MEIS data give a consistent picture, where deposited Au atoms are incorporated mainly in the second layer.

It is useful to compare this result with recent theoretical predictions using first-principles total energy calculations [13]. They show that a bilayer formation of Au on Ag(110) is unlikely to occur in thermal equilibrium and moreover that all of the Au atoms should be found in the second layer until all the Ag atoms are replaced. Therefore our observations below 1 ML appear to show the equilibrium growth of Au on Ag(110) rather than a kinetically limited process. Since the equilibrium growth on close-packed surfaces is different, as mentioned above, the open structure of the (110) surface must be responsible for atomic exchange [14] to take place.

The growth of Au on Ag(110) for coverage above 1 ML reveals 3D islands on top of the intermixed layers (fig. 1c). Since at 1 ML the top layer consists mainly of Ag atoms, Au atoms diffusing on the surface could either intermix with Ag atoms or stay on top to aggregate with other Au atoms. We have investigated these two possibilities quantitatively from calculations based on the MEIS and STM data. Quantitative agreement for $\theta \geq 2$ ML is found only if the Au grows essentially as pure Au fingers and islands on top of the surface. Therefore the surface can be composed of different structures: (1) bare Ag, (2) an intermixed layer which is mainly Ag on top of Au (Ag/Au), (3) Au on top of the intermixed layer (Au/Ag/Au), (4) Au/Au/Ag/Au, and (5) Au/Au/Au/Ag/Au. The relative composition of each of the above surface structures at any given coverage is determined by fitting the MEIS curves (fig. 1 in ref. [5]). The results of this analysis are shown in table 1 for different coverages. The same parameters are directly extracted from the STM data assuming that the 3D structures consist of gold only. This calculation has been performed mainly for $\theta = 1.4$ ML because all of the layers can be easily recognized in that case and the result is given in table 1. For higher coverages we can at least determine the fraction of the surface covered by islands and compare with the MEIS values given by table 1. In both cases there is a remarkable quantitative agreement between the numbers extracted from both techniques, demonstrating that the growth above 1 ML consists of 3D *gold* islands.

Finally, we have proven a very consistent model for the growth of Au on Ag(110). It can be called an "intermixed Stranski–Krastanov" growth mode: below 1 ML the gold atoms intermix with the silver atoms by being incorporated in the second layer, although some small amount may remain on the Ag(110) surface. Subsequently, 3D islands of gold grow on top of this Ag/Au layer. The shape, density and formation process of these islands are examined in the next section.

Table 1
Percentage of listed layers for varying Au coverage, as calculated in fit to MEIS experiment and measured from STM images (note agreement between MEIS and STM for 1.4 ML)

Au coverage (ML)	Percentage of listed layers				
	Bare Ag	Ag/Au intermix	Au/Ag/Au	Au/Au/Ag/Au	Au/Au/Au/Ag/Au
Fit to MEIS experiment					
1.0	12	75	13	0	0
1.4	0	64	24	12	0
2.0	0	31	41	19	9
2.3	0	21	44	17	18
STM data					
1.4	0	69	24	4	3

3.2. 3D islands

At ~1 ML fingers have started to grow from the steps (fig. 1a) and above 2 ML anisotropic 3D islands are observed (fig. 1c).

The shape, the size and the density of these islands are directly measured from the images. The length, the width and the average height of the islands versus their size are displayed in fig. 2. All of these parameters are increasing with the islands size while the length/width ratio is about constant (between 5 and 8). The island density is about $10^{10}/cm^2$. Atomic resolution images of the islands [12] show clearly that the islands are elongated along the direction of the [1$\bar{1}$0] close-packed rows. Thus, the rectangular shape of the islands reflects the anisotropy of the (110) substrate. One can imagine several causes for this anisotropic shape: anisotropic diffusion, anisotropic accommodation coefficient or anisotropic interactions. Simulations based on modified DLA models are still in progress but they suggest that anisotropic diffusion alone cannot account for the island shape. Such a conclusion was found for semiconductor Si islands on Si(100) [15]. The distinction between anisotropic accommodation coefficient and anisotropic interactions is made in order to distinguish between a kinetically limited growth shape and the equilibrium growth shape respectively. The issue could be adressed for example by studying the island shape versus annealing temperature.

At the coverage of 1.4 ML (fig. 1b), 3D structures are observed which reveal the transition in growth modes from 2D fingers to 3D islands. The top of these structures consists of a simple finger grown from the step whereas the bottom is always a multi-atomic step. Therefore correlated growth of 2D fingers from one terrace to another is responsible for these 3D structures.

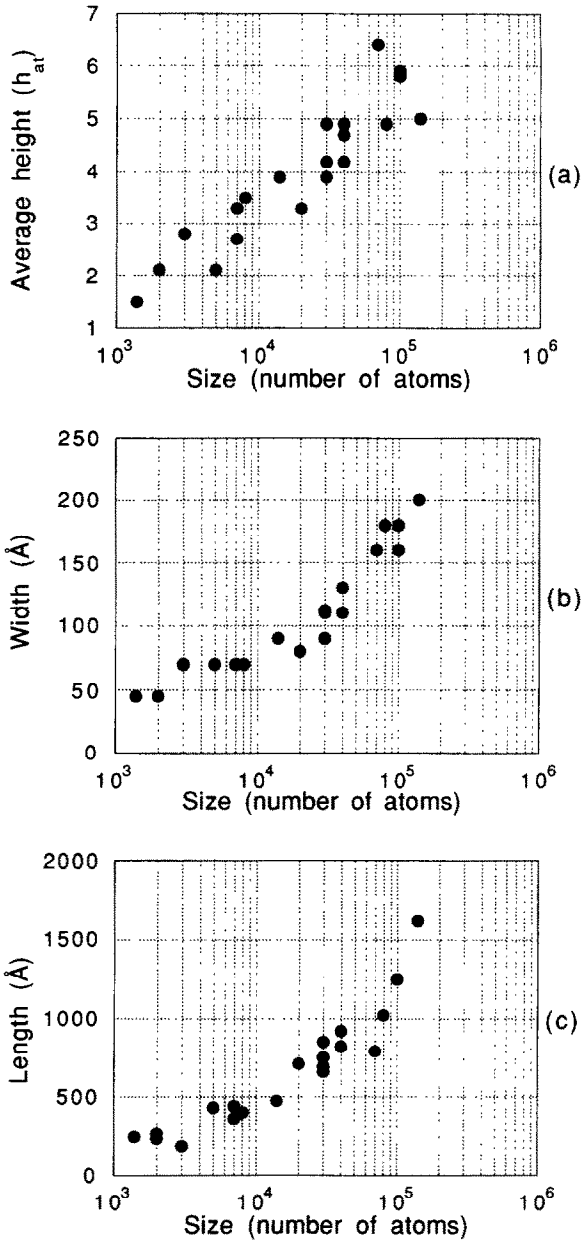

Fig. 2. Island shape parameters versus island size: (a) average height defined by maximum height/$\sqrt{2}$ – the monatomic step height h_{at} is 1.45 Å; (b) width; (c) length.

4. Conclusion

The first stage of the equilibrium growth of gold on the open fcc (110) silver surface is the formation of two intermixed layers: below 1 ML atomic exchange leaves almost all Au atoms in the second layer under a top layer of Ag. This behavior is attributed to the open structure of the (110) substrate. 2D alloying has also been observed on W and Mo bcc (100) substrates while not on densely packed bcc (110) surfaces [2]. By

modifying the surface energetics of Au/Ag(110), the intermixing process then gives rise to a SK growth mode rather than the expected FM mode, and 3D islands of gold are formed on top of the intermixed layers. The transition from 2D to 3D growth is shown to be due to the growth of correlated fingers at step edges.

Acknowledgements

We would like to acknowledge M. Altman for help in cleaning the Ag(110) sample, C.T. Chan and K.-M. Ho for sending preprints of ref. [13], R. Tromp for providing the MEIS Monte Carlo program, and helpful discussions with W. Egelhoff, J.H. Kaufman, and R.J. Wilson. This work was partially supported by the Office of Naval Research (N00014-89-C-0099).

References

[1] J.W. Matthews, Ed., Epitaxial Growth, Parts A and B (Academic Press, New York, 1975).
[2] E. Bauer, Appl. Surf. Sci. 11/12 (1982) 479.
[3] D.D. Chambliss, R.J. Wilson and S. Chiang, Phys. Rev. Lett. 66 (1991) 1721.
[4] D.D. Chambliss and R.J. Wilson, J. Vac. Sci. Technol. B 9 (1991) 928;
A. Brodde, G. Wilhelmi, D. Badt, H. Wengelnik and H. Neddermeyer, J. Vac. Sci. Technol. B 9 (1991) 920;
R.Q. Hwang, J. Schröder, C. Günther and R.J. Behm, Phys. Rev. Lett. 67 (1991) 3279.
[5] P. Fenter and T. Gustafsson, Phys. Rev. Lett. 64 (1990) 1142.
[6] P. Fenter and T. Gustafsson, Phys. Rev. B 43 (1991) 12195.
[7] S. Chiang, R.J. Wilson, Ch. Gerber and V.M. Hallmark, J. Vac. Sci. Technol. A 6 (1988) 386.
[8] G.W. Graham, Surf. Sci. 184 (1987) 137.
[9] R.J. Culbertson, L.C. Feldman, P.J. Silverman and H. Boehm, Phys. Rev. Lett. 47 (1981) 657.
[10] T.C. Hsieh, A.P. Shapiro and T.C. Chiang, Phys. Rev. B 31 (1985) 2541.
[11] J.F. van der Veen, Surf. Sci. Rep. 5 (1985) 199.
[12] S. Rousset, S. Chiang, D.E. Fowler and D.D. Chambliss, Phys. Rev. Lett. 69 (1992) 3200.
[13] K.P. Bohnen, C.T. Chan and K.M. Ho, Surf. Sci. Lett. 268 (1992) L284;
C.T. Chan, K.P. Bohnen and K.M. Ho, Phys. Rev. Lett. 69 (1992) 1672.
[14] P.J. Feibelman, Phys. Rev. Lett. 65 (1990) 729;
G.L. Kellogg and P.J. Feibelman, Phys. Rev. Lett. 64 (1990) 3143.
[15] Y.W. Mo, R. Kariotis, B.S. Swartzentruber, M.B. Webb and M.G. Lagally, J. Vac. Sci. Technol. A 8 (1990) 201.