Investigation of Iron on Gold Sub-Monolayer by Scanning Tunnelling Microscopy

Moftah A. Hussain[1], Mohammed M. Mohsen[2], Hassan A. Khairallal[3], Brijesh Kumar [4]
[1] *Head of the Department of Biomedical Engineering, Tobruk University, Libya*
[2]*Asst. Professor, Department of Biomedical Engineering, Tobruk University, Libya*
[3]*Asst. Professor, Department of Mechanical Engineering, Tobruk University, Libya*
[4] *Ph.D., Department of Medical Laboratory, Tobruk University, Libya*

Abstract **- Scanning Tunnelling Microscopy (STM) studies proved that the growth of Iron (Fe) on the gold (Au) (001)-hex surface was determined up to 0.4 monolayer (ML) by the enhanced diffusion along with reconstruction ridges. The reconstruction also determines the dimensions of the Fe islands. The growth is far from the equilibrium, which is not reached even within hours. As the coverage increases, the growth becomes to be influenced by the segregation of Au to the surface as postulated in earlier papers from atomic structure (AS). The segregation is closely connected with the vanishing of the Au reconstruction. The Au top layer, called the "self-surfactant layer", promotes the layer-by-layer growth of Fe. The mass transport observed during the growth and the Au segregation to the surface influences strongly the Au-Fe superlattices growth.**

Index Terms **- Epitaxial Thin Film Technology, Scanning Tunnelling Microscopy, Monolayer, Gold, Iron, Reconstruction, Super Lattices Growth.**

I.INTRODUCTION

Fe/Au films have promising applications in several engineering systems and have been adapted to fulfil a wide variety of functions [1]. Stride in thin films made to advance the development of energy storage devices. In such devices, the need for thin materially; high quality, reproducible characteristics and reliability have driven film growth technology through a rapid improvement of significant achievement [2].

Atomically flat single-crystalline Au substrates are necessary to grow Fe films and superlattices of high quality. Au single crystals can be used for this purpose, but they are expensive, and thus, they exclude ex-situ measurements. An alternative way to produce the substrate is to use single film technology. The usage of Au films is rather widely spread, but most applications relate to Au (111), which is the dense-packed face. It grows naturally on many single crystalline substrates and glass, as textured material [3].

This study aims to use surface coatings to protect structural materials in high-temperature environments is another thin film technology of enormous commercial significance also. The Fe/Au thin films are integral parts of many electronic systems designed to serve as memory devices, sensors, and actuators. Epitaxial technology demonstrating that the lattice parameter of the sub-monolayer (30 nm) thickness of Au under layer is dependent on its stress up to 2.66% in sub-monolayer (0.8 nm) Fe thin films evaporated on it.

II.METHODOLOGY

A. Preparation and Characterization number of the Au Buffer Layer:

From this point of view, this work (001) orientation is more difficult to grow, although the lattice match between Au (001) and MgO (001) is quite good. From the comparison of Fig. 1, we found that Au prefers (111) orientation when grown directly on MgO (001) at temperatures below 900K [4]. Even above this temperature, mixed (001) and (111) orientations are observed, and STM measurements proved that Au films grown at those conditions were discontinuous is also to note that only the cleaved MgO substrates give low carbon contamination. For the polished one, carbon was found not only on MgO but also on the surface of the Au films, independently of the substrate heat treatment [5].

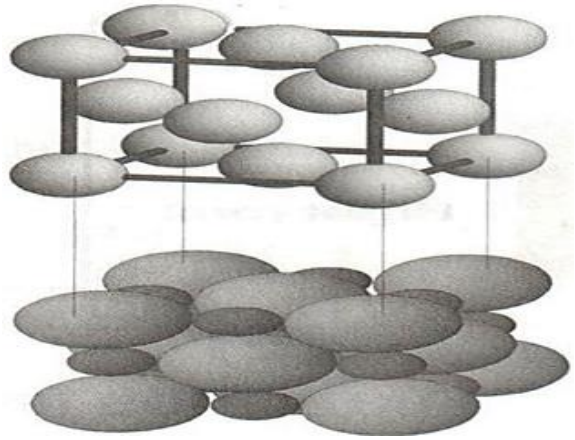

Figure 1, shows the growth of Au on MgO

The (001) orientation of Au can be forced by a thin Fe or Cr seed layer [6]. We use a 3nm Fe layer deposited at about 320 K on the MgO (001) which was pre-heated for 1h at 800K. The topography and the surface structure of the Au films (30nm was a standard thickness that ensured an electrical continuity) significantly depended on the deposition temperature and a thermal post-preparation treatment [3].

The micrometer STM scan of figure 2a reveals a certain feature of the MgO substrate, which is dominated by parallel cleavage steps. The smaller scan of figure 2b displays the high density of the elongated terraces running along with both (110) type-Au directions. The terraces are separated by monatomic steps, each of them being terminated by a pair of screw dislocations. The overall film roughness resulting from the observed up and down step sequence is rather high, about 0.8 nm over 1nm. The low energy electron diffraction (LEED) pattern of figure 2c reveals the reconstruction of the surface, which is roughly 5x1, the reconstruction is also visible on higher magnification STM scans. Through increasing the preparation temperature, the step becomes broader, but the film roughness doesn't decrease meaningfully. In order to make the film smoother they were annealed for 1h at 800 K, this procedure removes the reconstruction and changes the film topography dramatically as shown in figure 3a. The surface is flat over the areas corresponding to the MgO cleavage terraces (100-500 nm wide and 1-5 nm high). Monatomic steps are now irregular but also terminated by the screw dislocations. The roughness analysis yields the RMS value of the order 0.15 nm over 0.1 µm2 as documented also by the STM scan-section as shown in figure 3b.

In LEED (Fig.3c), we observe a 1x1 pattern which coincides with the atomic resolution image taken in the constant height mode is shown in figure 3d, where the square Au (001) lattice is visible. The strong fluctuations of intensity in the atomic corrugations are probably a reminder of the reconstruction.

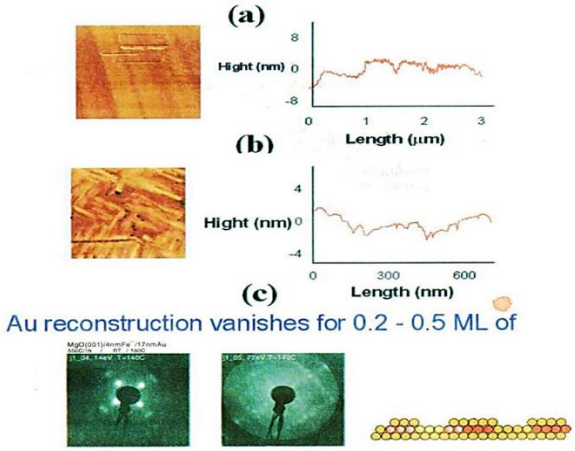

Figure 2, STM and LEED characterization of the AS prepared 30nm Au film deposited on 3nm Fe/MgO (001) at 450K. Next to the STM images, the height profiles along the indicated lines are shown: (a) 3x3µm2 topographic scan at the bias voltage VB=281 mV and tunnelling current 1=600 pA. (b) 643x643nm2 topographic scan at VB =281 mV, 1=600 pA. (c) LEED patterns at the electron energy as indicated.

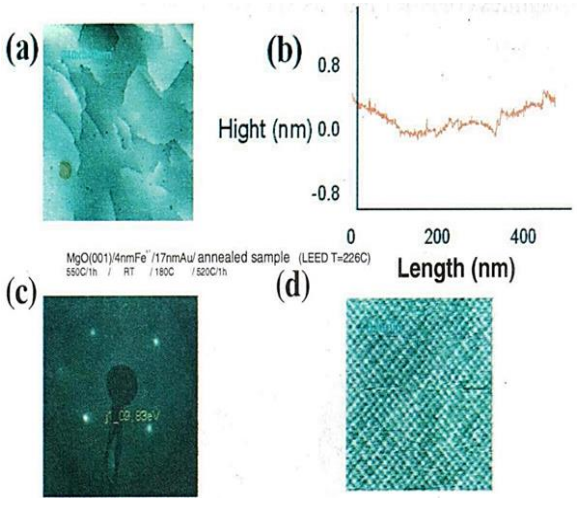

Figure 3, STM and LEED characterization of the 30nm Au film deposited on 3nm Fe/MgO (001) at 450K and annealed for an hour at 800K. (a) 340x340nm2 topographic scan at the bias voltage VB =480mV and tunneling current I=417pA. (b) height profiles along the indicated line. (c) LEED pattern at the electron energy as indicated. (d) Atomic resolution

8x8 nm2 constant height scan at VB =5mV, I =4.13nA.

Most of the previous iron growth studies on Au were done on reconstructed surfaces, which could be obtained also by thin-film technology in the following way; on the annealed 30 nm Au layer, a 3 nm Au layer was added at 450 K [3-7]. The resulting surface (RMS roughness over 0.1µm2) is shown in figure 4.

The most prominent features of the surface seen on large scans (Fig.4a) are straight or L-shaped steps, each of them terminated with a pair of screw dislocations seen better in figure 4b. The density of the dislocations is about 2x1010/cm2, resulting in flat regular terraces, which are on average 150 nm long and 20 nm wide. Other defects are small (about 6x6 nm2) square holes, with quantized sizes and edge dislocations disturbing the reconstruction ridges. The terraces and reconstruction ridges always run along (110)-type Au directions. The reconstruction, which is now seen clearly in the LEED pattern in figure 4c, is the same as for the bulk Au (001) surface roughly 5x1 (the ridges are spaced by 1.44 nm). At a higher magnification, in the constant height mode (Fig. 4d), the second modulation is visible with a period of about 8 nm. The origin of the reconstruction which has been intensively studied is the energy minimization by forming a quasi-hexagonal monolayer on the Au (001) surface [3-6]. The resulting 2.8x5 superstructure means that the surface layer is 20% denser than a 1xl layer. The reconstructed Au (001) surface will be denoted as Au (001)-hex. Four types of domains with the reconstruction ridges in the perpendicular directions are observed. The domains have different terminations, sometimes they meet and form a domain boundary at the same atomic level, and sometimes monatomic steps separate them.

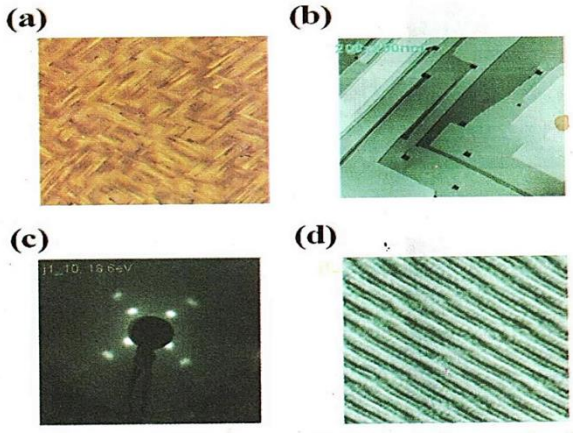

Figure 4, STM and LEED characterization of the standard Au buffer layer, prepared as described in the text, used for the Fe deposition. (a) Large topographic scan (2x2µm2) at the bias voltage VB=137 mV and tunnelling current I=434pA. (b) smaller scan (200x200nm2) showing the defect morphology. (c) LEED pattern at the electron energy as indicated. (d) Atomic resolution 13x13 nm2 constant height scan revealing details of the hex-type reconstruction.

B. Fe Growth on Reconstructed Surfaces:

The Fe deposition on the reconstructed Au surfaces was performed at 300K at the rate of about 1 ML/min. After the deposition, since the sample had to be transferred into the STM head. The preparation and the STM observation were time spaced typically by 1h. The typical STM scan parameters were 3mV of the base voltage and 0.5 nA of the tunnelling current.

The growth mode for the lowest coverage (0.13 ML and 0.20 ML) is similar. The Fe coverage determined from deposition time and rate agrees well with the value estimated from the island area in the STM images.

The large scan STM picture for Fe coverage 0.13 ML can be observed in figure 5. Islands are elongated in the direction of the reconstruction ridges, being the preferential directions of diffusion of the deposited atoms (islands). The reconstruction between the islands is maintained, there are also many small, dot-like islands. The islands tend to coalesce at the domain boundaries also at the steps. At this coverage, the square holes in the Au substrate do not play an important role. The scans are taken in intervals of 4 minutes, several hours after preparation.

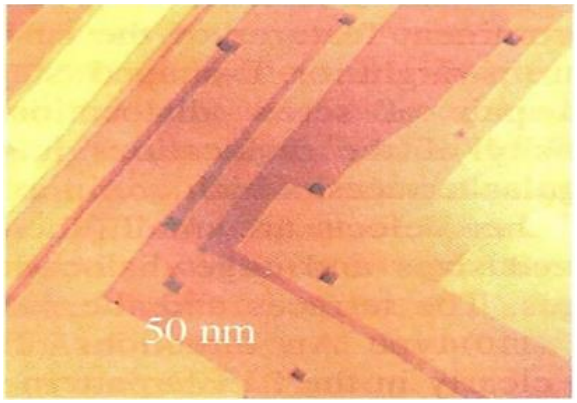

Figure 5, 200x200 nm2 scan in the topographic mode for 0.13 ML Fe coverage on the reconstructed Au (001) — hex surface.

Many of the islands show stripes (like double stripes), that are unstable on the time scale corresponding to the acquisition of the STM picture. The reconstruction close to the islands is unstable as well. Some of the smallest islands disappear, including it is difficult to judge how far the scanning tip induces the observed dynamic changes. However, a clear correlation between the number of scans and the time evolution was not observed.

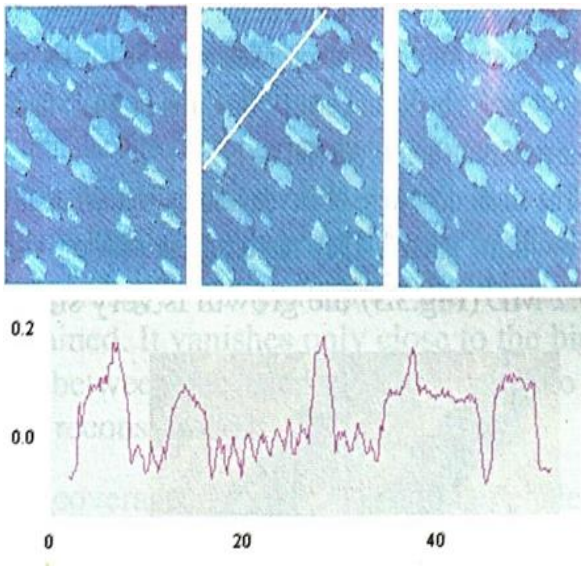

Figure 6, represents the sequence of four topographic scans (55x55nm2, 3mV, 1.3nA) for 0.13 ML Fe coverage on the reconstructed Au (001) hex surface taken in intervals of 4min. Arrow indicates vanishing dot islands. depth profile along the marked line allows identifying different structures, as described above.

Relying on the profile scans are shown in figure 6, the four different structures can be identified; (a) islands without reconstruction surrounded by the reconstructed areas, (b) islands without reconstruction surrounded by the non-reconstructed areas, (c) islands with stripes and double stripes, and (d) the histogram which confirmed the results as small dots. Based on the early literature, the rectangular islands at this coverage should be iron islands [8].

III.RESULTS AND DISCUSSION

The present studies indicate that the segregation of gold to the surface is closely connected with the disappearance of the reconstruction. The third observed type of the islands, namely the islands with stripes, can also be explained by involving the atomic place exchange between Au and Fe. The stripe-like features are too low to be the second Fe layer. They are probably rows of Au atoms incorporated in the Fe islands, similarly as it was observed by Radnik et al for Cu on Pt (001), which shows the same reconstruction as Au (001).

The small dots were observed like "igloos", which represent the smallest visible Fe aggregate (nuclei) of the critical size. It is still unclear whether the Fe atoms are on top or beneath the hexagonal Au layer. For Fe coverage 0.2 ML as shown in figure 7 the growth is very similar. Additional visible features are rectangular protrusions forming the second atomic layer on top of the island. Their height (about 0.15nm) corresponds to Fe (001) interlayer spacing [10].

These suggested that the Fe atom exchanges place with Au atoms immediately after reaching the surface. According to that, the gold atoms should be at the surface on every Fe coverage. Such interpretation by Herman et al. was necessary to explain the disagreement between the nominal coverage and that obtained from the STM picture.

In this work, the disagreement does not exist, and it is plausible that the islands are formed by the Fe atoms. The situation may be different for the islands which are surrounded by unreconstructed areas. The vanishing of the reconstruction means an excess of gold atoms, as will be explained below. It is seen from the profile scans that the height of the islands when in contact with unreconstructed areas, is very close to the Au (000) layer spacing.

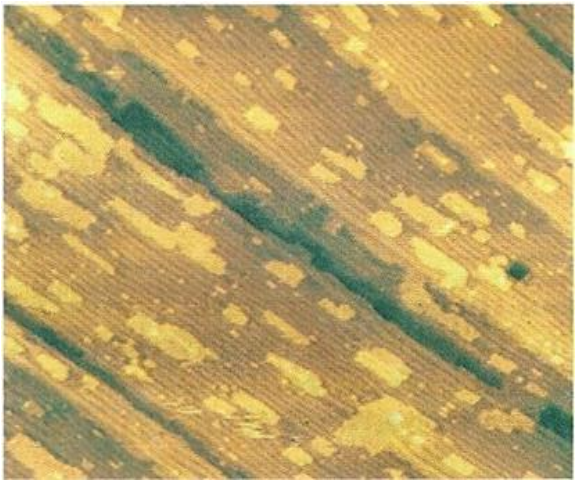

Figure 7, 100x100nm2 scan on the topographic mode for 0.2 ML Fe coverage on the reconstructed Au (001)—hex surface, VB=3mV, I=1.2 nA.

To summarizing, the Fe growth at low coverage is dominated by two competing processes. The first one is the nucleation of small Fe nuclei, which are pinned to the reconstruction ridges. The size of nuclei is quantized with the reconstruction. The islands with the smallest observed width cover the highest part of the reconstruction ridges (three atomic rows). Most of the smallest islands are dot-like and contain about 10 atoms; a few have double or triple-dot lengths.

The second important process is an enhanced diffusion along the reconstruction rows. The number of the dot islands decreases with time elapsed since the preparation. Obviously, they diffuse easily along the reconstruction ridges and join bigger islands. Islands are always elongated in the direction of the reconstruction ridges due to the preferential diffusion, except those formed at the domain boundaries, where two perpendicular diffusion directions meet. The large islands at the domain boundaries are probably special features of our thin film, Au substrate, and its reconstruction domain morphology. In principle, the reconstruction between islands is retained. It vanishes only close to the biggest islands or if the distance between the islands is too small to allow a longer period of reconstruction. At the coverage of 0.4 ML (Fig. 8), the coalescence dominates the nucleation. Thus, elongated islands join to form long chains.

The irregular islands at the domain boundaries become huge, whereas often decorated by the second layer small islands. The reconstruction still exists in the uncovered area, nonetheless it pushed away from the islands. The STM images change considerably by time is shown in figure 9 (a-b), taken subsequently (the time gap is several minutes). The second layer "dissolves" and the islands grow at its cost, this process reduces the reconstructed areas. For the reconstructed quasi-hexagonal Au layer, the vanishing of the reconstruction means an excess of the Au atoms because the non-reconstructed layer is 20% less dense than the reconstructed one. We assume that the segregation of Au to the surface is closely connected with the disappearance of the reconstruction. The process starts at just about 0.4 ML. The highly unsettled state, which is characterized by atomic motion and mass flow helps in reaching the equilibrium in which Au covers the Fe islands, preventing three-dimensional growth.

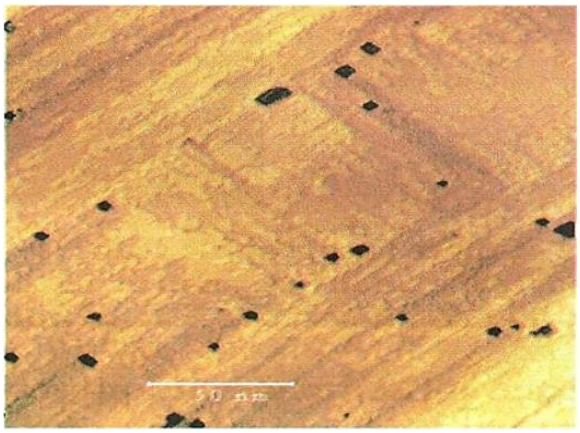

Figure 8, 200 x200 nm2 scan on the topographic mode for 0.4 ML Fe coverage on the reconstructed Au (001) —hex surface, VB=3mV, I=lnA.

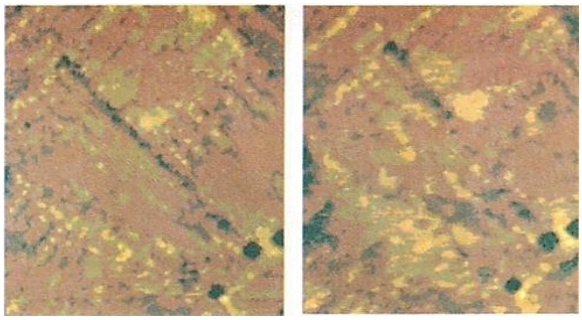

Figure 9, Sequence of three topographic scans (90 x90 nm2, 3 mV, 1.3nA) for 0.4 ML Fe coverage on the reconstructed Au (001) — hex surface taken in intervals of several min.

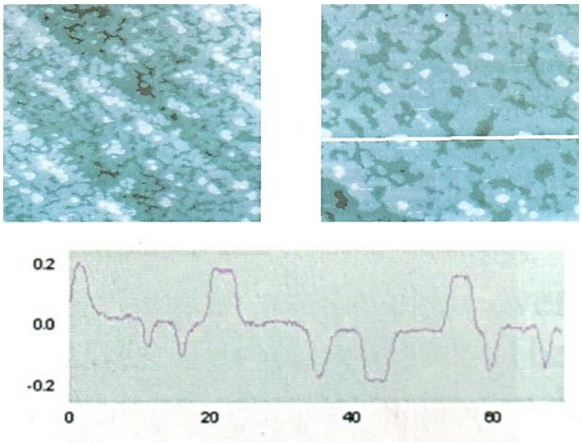

Figure 10, (70 x 70 nm2) topographic scans for 0.13ML Fe coverage on the reconstructed Au (001) — hex surface. Two images (a & b) are chosen to show the different size scales of the pit structure. (c) histogram illustrates that in-depth profile along the marked line only 0.2nm level difference is seen.

The Fe islands cannot be identified the growth, which is close to layer by layer one. Only two atomic layers

are involved in the growth. Due to the percolation in the first atomic layer, we analyze pits rather than an island structure. The pit size is different as a remainder of the different island kinds observed at lower coverage; the elongated one on terraces (Fig. 10a) and the irregular but considerable one at the domain boundaries (Fig. 10b). Only three atomic levels are seen on terraces (the histogram in Fig.10c.). They are equally spaced by 0.2nm, very close to the value of Au (001) layers.

Assuming that the areas elevated above the Au substrate are due to the Fe atoms, we obtain the Fe coverage which exceeds the one obtained from the quartz monitor. It is an indication that the observed surface morphology is not only due to the Fe adsorbate, but it comes also from an excess of Au that was released by the vanishing of the reconstruction.

The question remains open, to which extent the observed pit and island structure corresponds to Fe, to Au or to an intermixed layer. The atomic resolution images presented in figure 11, for this sample a square two-dimensional periodicity did not reveal any chemical contrast, which could help in solving the above question. The situation is very similar for thicker films, which do not differ in surface topography displayed by the STM from 0.65 ML.

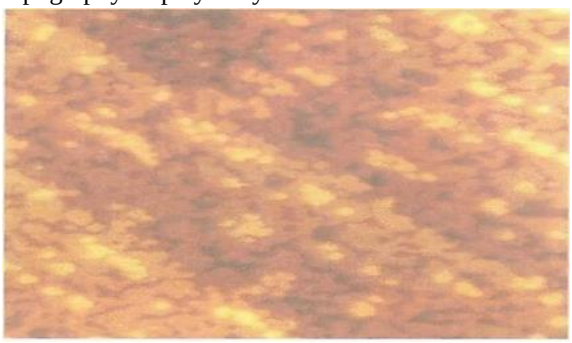

Figure 11, Atomic resolution 10x10 nm2 constant height scan for 0.65 ML Fe coverage on the reconstructed Au (001) -hex taken at VB=2mV and 1=3 nA.

Figure 12, (50 x 50 nm2) topographic scans for 0.65 ML Fe coverage on the reconstructed Au (001) — hex surface. After annealing for 0.5 h at 600K.

In the literature, it is reported that Fe films become smoother when annealed [3]. Indeed, the STM reveals a change in surface topography for the film 0.65 ML Fe that was annealed for 30 min at 600K are shown in figure12.

The pit edges become sharper and straight, and the overall surface roughness is significantly lowered because the areas of the same height are by order of larger magnitude. However, from the STM picture, it is not obvious that the smoothing of the surface is due to the smoothing of the iron layer.

IV.CONCLUSION

The STM studies proved that the growth of Fe on the Au (001) hex surface is determined up to 0.4ML by the enhanced diffusion along the reconstruction ridges. The reconstruction also determines the dimensions of the Fe islands. The growth is far from the equilibrium, which is not reached even within hours. As the coverage increases, the growth becomes influenced by the segregation of Au to the surface as postulated in earlier papers [3-4].

The segregation is closely connected with the vanishing of the Au reconstruction. The Au top layer, called the "self-surfactant layer", promotes the layer-by-layer growth of Fe. The mass transport observed during the growth and the Au segregation to the surface influences strongly the Au-Fe superlattices growth.

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