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STUDIES IN NaCl CRYSTAL SURFACES DURING THEIR EVAPORATION IN AIR AND THEIR CHEMICAL DISSOLUTION*

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RESUMEN

Usando el método de decoración con oro[1], *se observaron escalones producidos en las superficies (100) de cristales de NaCl durante su evaporación en aire y durante su disolución química con el reactivo de Moran. La evaporación en aire se realizó a 580°C durante 15 y 90 minutos respectivamente. En la evaporación durante 15 minutos, se observaron estructuras concéntricas de escalones monoatómicos. Con este tiempo de ataque, los escalones son cerrados y sus distribuciones son estables. También se observaron estructuras de escalones no*

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concéntricos las cuales se atribuyen a movimientos de las fuentes. Para la evaporación durante 90 minutos, se produce inestabilidad en las distribuciones de escalones lo cual da lugar a la formación de macroescalones. También son observadas estructuras cuya parte central esta libre de escalonès; esto es explicado en términos de la aniquilación de la dislocación fuente. Para la disolución química se presentan las estructuras de escalones típicas, las cuales se caracterizan por la forma inhomogénea en que el oro se nuclea a lo largo de los escalones. Esto es probablemente debido a un envenenamiento de los "kinks". Algunas otras características de las estructuras de escalones, para ambos tipos de ataque, también son discutidas.

ABSTRACT

Using the method of gold decoration[1], steps produced in (100) NaCl crystal surfaces are observed. The steps were developed on crystals during evaporation in an impure medium (air) and during chemical dissolution with Moran's reagent. Evaporation in air was performed at 580° C during 15 and 90 minutes, respectively. For 15 minutes evaporation, concentric monoatomic step structures are observed. The steps are closed and their distribution is stable. Non concentric step structures are also present. We attribute this to the motion of the step sources. For 90 minutes evaporation time, the step distribution became unstable causing the formation of macrosteps. Structures whose center is free of steps, are also observed and this is discussed in terms of annihilation of the step source. For the chemical dissolution, typical step structures are present. The nucleation of gold in the steps is not homogeneous, probably due to a poisoning of the kinks. Some other characteristics related to the step structures, for both etching types, are also discussed.

I. INTRODUCTION

The explanation of some phenomena that occur in a single-crystal surface during its growth, its evaporation or its dissolution, is based on the existence of steps of atomic height on the surface. The formation of these steps, their relative position as well as interaction with impurities, etc. determine the dynamics of surface growth, evaporation or dissolution. Experimental observation of these steps has been done by means of gold decoration[1]. Betghe and Keller[2] studied phenomena that occurred on NaCl crystals during vacuum evaporation by means of the decoration technique and they found monoatomic step structures in spiral form. The principal characteristic of these structures is the stability in the step distributions. In this paper NaCl crystal evaporation is studied in an impure medium-air at atmospheric pressure as well as its chemical dissolution with a saturated reagent using gold decoration.

II. EXPERIMENTAL TECHNIQUE

Gold decoration consists mainly in depositing small amounts of gold (5-10 Å) on a crystal surface while this is maintained at temperatures between 100°C and 300°C. The metal particles migrate by diffusion over the surface until they are trapped by higher-energy sites. These sites, which are named equivalent sites, are generally kinks which are present in monoatomic steps. When a particle is trapped, it induces the addition of other particles until a nucleus, which is visible in the electron microscope, is formed. In the surface regions where there are no steps, random nuclei are formed by gold vapor supersaturation.

In this work, decoration was done on (100) NaCl crystal surfaces under different etching conditions: a) Surfaces etched thermally in air at 580°C for 15 and 90 minutes, respectively, and b) surfaces etched chemically with Moran's reagent (ethyl alcohol at 98% saturated with $HgCl_2$) during one or two seconds. Both types of etching are so gentle that they only remove some atomic layers. In order to observe the surfaces in the electron microscope they were carbon replicated in the usual form[1].

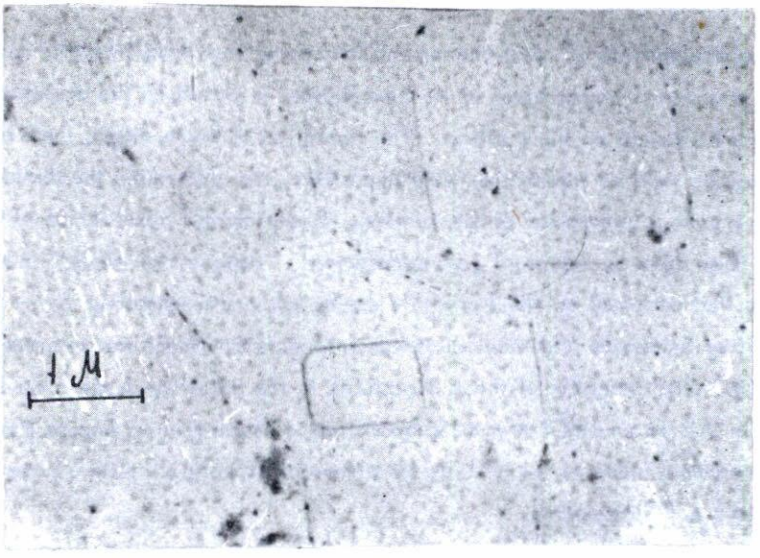

Fig. 1 Interaction between monoatomic steps produced in air evaporation (580°C during 15 minutes).

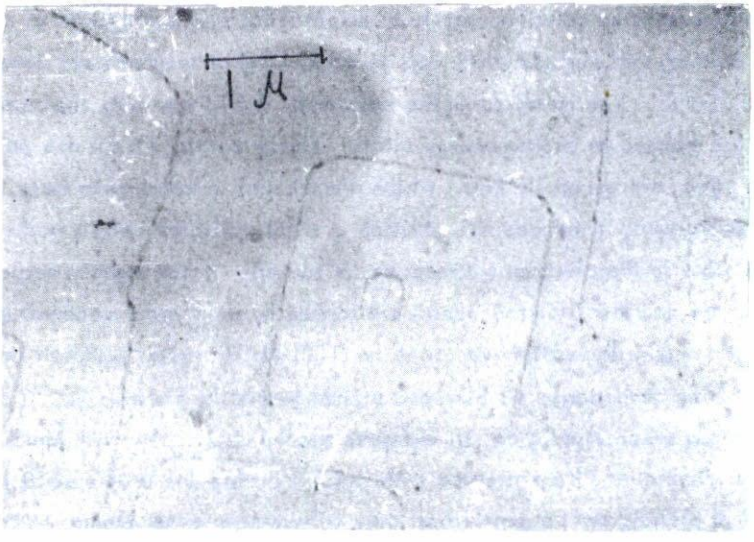

Fig. 2 Non-concentric step structure in air evaporation (580°C during 15 minutes).

III. AIR EVAPORATION

When thermal etching was carried out in air at 580°C for 15 minutes, concentric closed step structures were observed. Although the steps mostly show a square shape, the rectangular shape is also observed. Step structures appear with a mean density of 10^5 per cm^2. Figure 1 shows the interaction between two steps from different structures. Two steps of opposite sign moved in opposite directions, annihilating each other when they met. Thus, in evaporation in an impure medium, monoatomic steps are produced as in the case of vacuum evaporation. The principal characteristics in monoatomic step structures produced in air evaporation during 15 minutes are the following: a) the steps are closed, b) the step distributions are stable. Non-concentric step structures can also be found. We think that the latter type of structure is due to the motion of the step source, which emits steps at different points. Possibly, the source motion is due to thermal fluctuations. There are apparently two directions along which the sources moved, relative to the steps that were emitted before by them; one direction parallel to the sides of the steps, and the other along the diagonals. Figure 2 shows a parallel movement along the sides.

When the etching time is increased to 90 minutes the step distributions become unstable. This instability produces monoatomic steps that reach each other and form macrosteps. This phenomenon is described in detail in another paper[3]. The predominant shape of closed steps is now rectangular. This is due to the instability in the step distributions which results in variations in the velocity of step advance.

In 90 minutes etching time the center of some of the step structures is free from steps as shown in Figure 3. That is, the step source suddenly stops emitting. This may be due to the annihilation of the source dislocation when it interacts with another dislocation at the same plane, and such that its stress field is cancelled with that of the source dislocation[4].

On the other hand, the step-structure density remains constant (10^5 per cm^2); that is, it does not depend on the etching time. When etching is done at higher

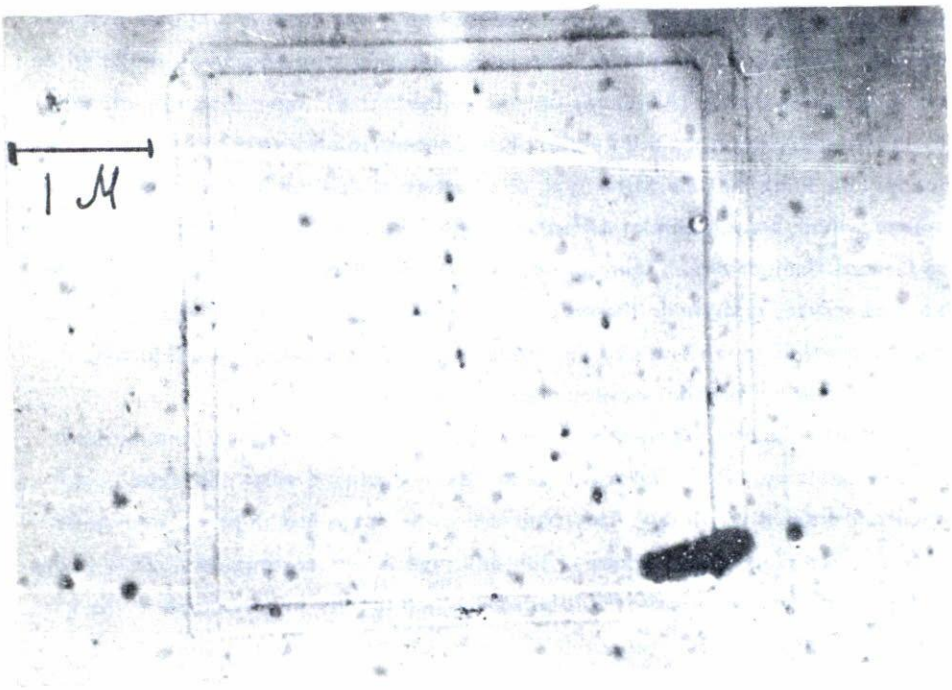

Fig. 3 Step structure with the center free of steps (580°C during 90 minutes).

temperatures, the above step structures originate macrosteps, like those described by Torres, Alvarez and Reyes[5]. The principal characteristics of the evaporation in an impure medium are summarized in table I.

IV. CHEMICAL DISSOLUTION

In surfaces etched chemically with Moran's reagent for one or two seconds, step structures are produced. Chemical dissolution of the crystal takes place by a movement of the steps in a direction opposite to that of its growth. A typical pattern of the step structures is shown in Figure 4. According to Chernov[6] the sources of the steps are screw dislocations, two-dimensional nuclei of dissolution, sub-grain boundaries, and the crystal edges. The shape of the step structures depends on the ratio V_n/V_t of the normal dissolution rate to the tangential velocity of the steps. In our case the value of V_n/V_t is small and this produces shallow step structures. The mean density of the step structures is 10^6 per cm^2.

In Figure 5 it can be observed that there exists a zone free of steps formed when two sources are close to each other; the steps annihilate each other as they interact. This shows again that the steps are probably monoatomic.

Gold nucleation along the steps is not homogeneous, as can be seen in Figures 4 and 5. This could be explained in the following form: The reagent impurities are adsorbed when the reagent comes in contact with the crystal. The impurities adsorbed have a short lifetime on the surface, and the active sites of dissolution (kinks) tend to trap the impurities[6]. In this way, a distribution of impurities is produced along the steps. Under these conditions the equivalent sites for gold nucleation will decrease in number when the crystal is decorated and a non-homogeneous nucleation will be produced.

An interesting characteristic of the step structures is that the steps near the source present rounded edges, while the steps far from the source have straight edges. The reason for this is not obvious, although it is very probable that this effect is related to the concentration of impurities of the reagent.

	Air evaporation at 580°C during 15 minutes.	Air evaporation at 580°C during 90 minutes	Chemical dissolution with Moran's reagent for two seconds
Step heights	monoatomic	monoatomic and macrosteps	very likely monoatomic
Step distributions	stable	unstable	stable
Step shape	square and some rectangular	rectanaular	open steps with rounded edges near the source
Gold nucleation	homogeneous	homogeneous	inhomogeneous
Step source	motion of the sources	motion of the sources	sources remain fixed
Density of step structures	10^5 per cm^2	10^5 per cm^2	10^6 per cm^2

Table I Comparison between steps produced in air evaporation at 580°C and in chemical dissolution with Moran's reagent of NaCl surfaces

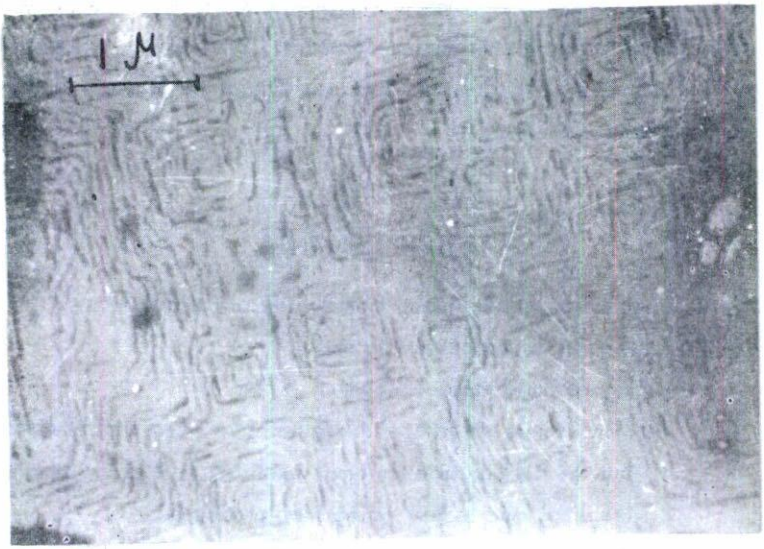

Fig. 4 Step structure of chemical dissolution with Moran's reactive during two seconds.

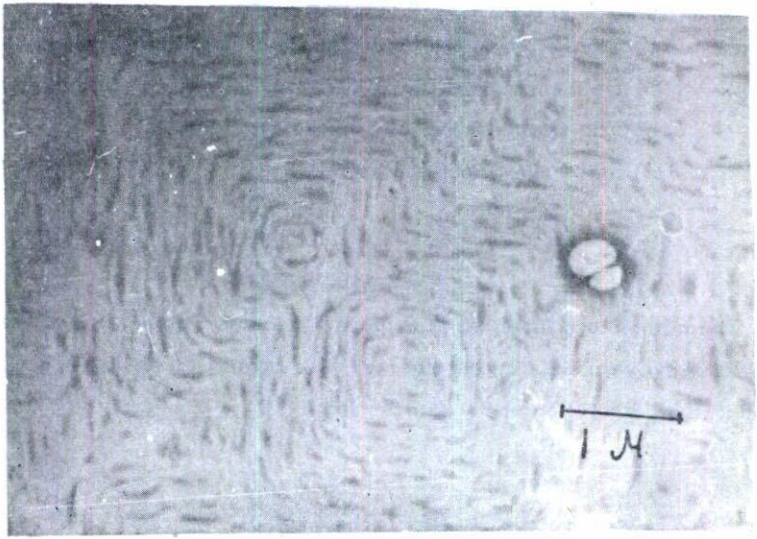

Fig. 5 Interaction between two step structures produced during chemical dissolution with Moran's reactive during two seconds.

Stability in step distributions is shown in chemical dissolution and the relative distance between steps remains constant. The step source remains fixed at the center of the step structure. Macrosteps cannot be formed under these etching conditions (see table I).

I. CONCLUSIONS

The following can be concluded from the experimental data;

1. In air evaporation we observe that:
   a) Monoatomic steps occur
   b) Monoatomic steps at the beginning are in a stable distribution but the distribution becomes unstable as etching time is increased, macrosteps being then produced.
   c) The mean density of step structures is independent from etching time.
   d) All steps present closed structures.
2. In chemical dissolution we may say that:
   a) The height of the produced steps is probably monoatomic.
   b) Gold nucleation along the steps is not homogeneous.
   c) The step distributions are stable.
   d) Steps show open structures.

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