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The Influence of Orientation and Crystal Defects on the Catalytic Activity of Silver

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The rate of the catalytic decomposition of formic acid to hydrogen and carbon dioxide has been measured in the zero order range on silver crystals to study the influence of surface structure and crystal defects. The value of the activation energy varies between 18 and 32 kcal/mole, depending upon the orientation of the surface. Compensation occurs to give similar rates for all surfaces. The behavior of evaporated films ({111} and {100}) and bulk single crystals, sputtered and thermally etched, fits consistently into a model in which the activation energy for the reaction depends upon the stability of the chemisorbed species, which in turn is influenced by the degree of unsaturation of surface atoms. Variations of concentrations of crystal defects have no influence on the rate of the reaction.

Introduction

In studying how defects and surface structure influence the catalytic behavior of solids, it is esential to use catalysts with well-defined surfaces, and the reaction must therefore proceed reproducibly and with sufficient speed on rather small surface areas. A widely studied reaction, suitable for this purpose, is the catalytic decomposition of formic acid, which usually proceeds on metals by dehydrogenation, i.e.,

$$HCOOH \rightarrow H_2 + CO_2$$

In a previous investigation, this reaction was studied on polycrystalline and epitaxed single crystal films of silver (*1*). It was concluded from that work that the value of the activation energy depended on the proportion of the surface which was flat and parallel to a (111) plane, but was not sensitive to the concentration of defects in the crystals. However, the only single crystals studied were {111} films and, furthermore, the influence of isolated dislocations was not clearly established because their concentrations ($10^9 - 10^{10}$ cm^{-2}) did not vary sufficiently. It seemed desirable therefore to obtain information about the catalytic activity of flat surfaces of other orientations and to study further the influence of defects in the catalysts. Other workers have concluded or suggested that active sites for the decomposition of formic acid are dislocations on silver (*2*, *3*, *4*), vacancies on platinum (*5*), and dislocations, vacancies, or vicinal planes on gold (*6*).

In the present work, this reaction was studied on {100} and {111} films of silver epitaxed on rocksalt and mica, respectively; a variation of the thickness of the films gave a greater variation of defect concentration than before. The activation energy and the pre-exponential factor for the reaction were derived from rate measurements at temperatures in the range 180° to 260°C. These results are compared with the catalytic behavior of bulk single crystals, cleaned by sputtering and thermally etched to produce (111) or (100) facets. The defect concentrations in the catalysts were determined by electron microscopy, and the films on mica were examined in sufficient detail to determine the distribution of Burgers vectors of the dislocations. The surfaces were examined using shadowed and decorated replicas.

Altogether the specimens provided a series of different surfaces containing either (111) or (100) planes, and the concentration of crystal defects varied between types of specimens by several orders of magnitude.

Experimental Methods

Materials

Formic acid. Formic acid (98 — 100% AR) was distilled over phosphorous pentoxide and then purified by recrystallization until the melting point was 8.4° ± 0.1°C. It was stored under vacuum at —70°C and distilled into the reaction system immediately before the catalytic measurements.

Silver. Spectroscopically pure silver (Johnson-Matthey, 99.999%) was used for the preparation of the films as well as for some of the bulk single crystals grown from the melt.

Substrates. Selected pieces of mica (Australian muscovite) were cut to size (1.5 × 3.0 cm) and cleaved just before being placed into the deposition chamber.

Good cleaving quality rocksalt blanks (3.0 × 2.0 × 1.0 cm) from Harshaw Chemical Co. were cleaved into smaller pieces and those with smooth surfaces were selected for deposition of {100} films (surface area approximately 6 cm^2).

Preparation of Catalysts

All films were continuous and were deposited in vessels which could be evacuated to $<1 \times 10^{-6}$ torr by mercury diffusion pumps trapped with liquid nitrogen. The deposition of silver crystals on the edges and backs of the substrates was prevented by shields.

Films on rocksalt. These films were deposited in a glass vessel (*1*). The silver charge, cleaned in dilute HNO_3 and washed in distilled water, was vacuum-melted onto a tantalum filament; the vessel was then cut open and, after introducing the rocksalt substrate, it was sealed by glass-blowing and reevacuated. The substrate was heated to 400°C and then a 1000 Å thick film deposited (rate 30–80 Å/sec) at a pressure of 1×10^{-5} torr. The films were annealed in situ at 400°C for 30 min, cooled to room temperature, and transferred through the air to the catalysis apparatus.

Films on mica. Films about 10 000 Å thick were prepared in a glass bell-jar by depositing a film about 1500 Å thick (rate 80 Å/sec, pressure 5×10^{-6} torr) onto mica heated to 350 — 380°C. The film was annealed immediately at 450— 480°C for 1 hr, and, after reducing the temperature to 400°C, the thickness was increased to 10 000 Å by further deposition. The film was then annealed for more than 1 hr at 650°C (pressure 5×10^{-5} torr) and cooled slowly to room temperature.

Thin films (1000 Å) were prepared in the bell-jar with the substrate at 280°C and were not annealed. Previously such films were designated Type III (*1*).

Bulk single crystals. Crystals (2 × 6 × 0.1 cm) were grown from the melt (pressure about 1×10^{-5} torr) in a mold of pure high-density graphite. Those with orientations within 10° of the [111] and [100] poles were selected for the catalytic measurements and were etched in dilute HNO_3 and then either chemically polished with a solution of Cr_2O_3 + HCl (*7*) or electropolished in a cyanide bath (*8*). Both methods gave smooth surfaces but left a surface film which was removed by sputtering with argon ions in a glow discharge for 20 min at 4 ± 0.5 kV and a total discharge current of 0.5 — 0.8 mA. The argon pressure was 1×10^{-2} torr and the temperature of the crystals rose to between 450 — 650°C during sputtering.

After the catalytic measurements, the crystals were thermally etched for several days at 930 — 950°C in a vertical tube furnace of recrystallized alumina open to the air, but plugged loosely on both ends with fine silver gauze. The crystals were then cooled slowly to room temperature and the catalytic measurements repeated.

Rate Measurements

The rate measurements and the annealing in the reaction vessel were carried out as described previously (*1*), using the same static system, except that the mercury dif-

fusion pump was replaced by a two-stage oil diffusion pump charged with "Diffelen Ultra" (Leybold Nachf.). The measurements were restricted to the zero order range, i.e., temperatures of 180–260°C, and formic acid pressures of 63 torr. Corrections for the reaction on glass walls and on the areas of substrates not covered by silver were determined from rate measurements in the presence of substrate blanks.

Examination of the Catalysts

The catalysts were examined optically, and by electron microscopy in an Elmiskop I operated at 100 kV. The appearance of the various crystal defects (grain boundaries, stacking faults and coherent twin boundaries, noncoherent twin boundaries, and dislocations) in electron micrographs and the way in which their concentrations can be measured have been discussed previously (*1*).

Replicas of the surface were made by shadowing with platinum-carbon at an angle of 20° or by decorating with about 10 Å of gold to reveal surface features (*9*). The limit of sensitivity of shadowing is about 20 Å for abrupt changes in surface level, but with decoration even monatomic steps can be identified (*10*, *11*).

Films to be examined by transmission electron microscopy were stripped from rocksalt with water and from mica with hydrofluoric acid. Being too thick for transmission, the 10 000 Å thick films were thinned by electropolishing. In order to retain the defects intersecting the reacting surface, silver was removed only from the side adjacent to the substrate. Specimens were tilted in the electron microscope to obtain suitable diffraction conditions for examination and identification of defects. In micrographs of {111} films taken with $\bar{2}02$, $\bar{2}20$, $02\bar{2}$ reflections, only dislocations visible with all these reflections have Burgers vectors parallel to the (111) plane of the surface.

Thick films containing low concentrations of defects were etched in a solution of $NH_3 + H_2O_2$ (*7*) and the pits in the surface examined in replicas at a magnification of about 2000×. Transmission electron micrographs taken after etching showed that pits formed preferentially at the ends of stacking faults and coherent twin boundaries, but not where dislocations emerged at the surface. Noncoherent twin boundaries in certain directions were also etched (*12*).

The concentrations of defects are expressed as total length of boundaries or as the number of lines (in case of dislocations) intersecting unit surface area of catalyst. The concentrations of stacking faults and coherent twin boundaries are quoted together, because they are very similar, and it is difficult to distinguish overlapping faults from thin twins. The partial dislocations associated with these two defects are not quoted, but their concentrations are roughly proportional to the total length of these defects.

Results

Catalysis

The initial rate measurements on each specimen were carried out at high temperatures in order to equilibrate the surface structure. The films usually had, at first, a very high activity (up to ten times the equilibrium rate) which decreased and became constant after two to three rate measurements. The variations of rates with temperature were then reproducible and reversible and only these values were used to calculate the results in Tables 1 and 2.

Sometimes rates were lower when a specimen had been left in the reaction vessel overnight, but catalysis at high temperatures usually restored its activity. If this was not the case, the catalyst was discarded.

Small amounts (about 5% of the total) of carbon dioxide, carbon monoxide, hydrogen, and water were produced by the reaction on the glass walls and substrate blanks. After correction for these, it was found that the reaction on silver produced only hydrogen and carbon dioxide. The values of log (rate) were plotted against $1/T$ °K and all catalysts gave straight lines within the experimental accuracy. The experimental activation energy E (kcal/mole) and the logarithm of the pre-expo-

TABLE 1
VARIATION OF E AND LOG A FOR {100} AND THICK {111} FILMS ON ANNEALING

Catalyst	Before anneal at 400°C		After anneal at 400°C	
	E (kcal/mole)	log A (A in molecules cm^{-2} sec^{-1})	E (kcal/mole)	log A (A in molecules cm^{-2} sec^{-1})
{111} 10000 Å	26.7	26.5	21.7	23.5
	26.0	26.2	23.5	24.6
	24.8	25.5	18.1	22.5
	26.2	25.7	21.9	23.5
	25.7	26.5	18.9	22.4
Mean values	25.8	26.1	20.8	23.4
{100} 1000 Å	24.9	25.7	25.9	26.1
	27.3	26.7	28.6	27.3
	29.1	27.3	27.6	26.3
	26.1	26.0	26.2	26.0
Mean values	26.8	26.4	27.1	26.4

nential factor A (molecules/cm^2 sec) were derived from the Arrhenius plot by the method of least squares. In calculating the values of A, the area of the catalyst was taken as its projected geometric area. The 95% confidence limits for the results on a given film are ±1 kcal/mole for E and ±0.3 for $\log_{10} A$. The values for E and $\log_{10} A$ before and after annealing of {100} and thick {111} films are given in Table 1, and the mean values of E and $\log_{10} A$ together with the average concentrations of defects in different types of catalysts are summarized in Table 2. For easy comparison, previous results on polycrystalline silver films on glass are included (*1*).

As found previously (*1*), a high value of E was always accompanied by a high value of A, and a straight line fitted to a plot of E versus log A gave the equation

$$\log_{10} A = 14 + 0.47E$$

Thus all catalysts exhibited a compensation effect (*13*).

Films

The thin {111} films behaved in the same way as previously [Type III (*1*)] and the values of E and A in Table 2 are the averages of the new and old measurements. On annealing, the mean value of E dropped from 26.8 to 20.8 kcal/mole. The values in Table 1 show that the five thick {111} films showed similar decreases. Before annealing, E was slightly lower but after annealing was the same as that of thin {111} films.

The values of E and A of the {100} films were, before annealing, in the same range as those of the unannealed {111} films, but these values did not change on annealing.

Apart from the {100} films listed in Table 1, a number of other films on rock-salt were obtained which were predominantly {100}, but which contained {111} grains. These showed an average decrease in E on annealing of 3.8 kcal/mole (from 26.6) which was less than that of {111} single crystal films. Correspondingly log A decreased by 1.8 from 26.2 to 24.4.

Bulk Single Crystals

In some previous experiments (*14*), twelve single crystals (99.97% purity) of random orientations with sputtered surfaces were tested as catalysts in a flow apparatus and all had the same activity. They gave a mean value of $E = 31.5$ kcal/mole and a maximum deviation of ±2.5 kcal/mole. Thermal etching lowered E by about 8 kcal/mole to a mean value of 23.8 kcal/mole when the new surfaces exposed (111) facets, but only by about 2 kcal/mole when (100) facets occurred (mean value 29.9 kcal/mole).

TABLE 2

AVERAGE CATALYTIC CONSTANTS AND STRUCTURAL FEATURES OF DIFFERENT TYPES OF CATALYSTS

	Catalyst	Concentrations of Defects				Fraction of flat (111) or (100) in surface (%)	E (kcal/mole)	ΔE (kcal/mole)	$\log_{10}A$ (A in molecules cm^{-2} sec^{-1})	$\Delta \log_{10}A$
		Grain boundaries (cm^{-1})	Stacking fault and coherent twin boundaries (cm^{-1})	Noncoherent twin boundaries (cm^{-1})	Isolated whole dislocations (cm^{-2})					
1	{111} 1000 Å (thin)	0	5×10^3	1×10^4	10^9–10^{10}	75–85	26.8	6.0	26.8	3.3
1a	Annealed	0	3×10^3	0	10^9–10^{10}	95	20.8		23.5	
2	{111} 10000 Å (thick)	0	4×10^2	1×10^3	10^8	80	25.8	5.0	26.1	2.7
2a	Annealed	0	4×10^2	1×10^3	10^8	95	20.8		23.4	
3	{100} 1000 Å	0	2×10^4	0	10^{10}	<100	26.8	0	26.4	0
3a	Annealed	0	6×10^3	0	10^9	<100	27.1		26.4	
4	{100} + {111} 1000 Å	10^2–10^3	2×10^4	0	10^{10}	<100	26.6	3.8	26.2	1.8
4a	Annealed	10^2–10^3	6×10^3	0	10^9	<100	22.8		24.4	
5	Polycrystal on glass	3×10^4	7×10^4	0	$\sim 10^9$	15	27.3	0	26.6	0
5a	Annealed	3×10^4	3×10^4	0	$\sim 10^9$	8–15	27.1		26.8	
6	Bulk single crystal random	0	0	0	10^7	0	31.5	7.7	28.5	3.7
6a	Thermally etched (111)	0	0	0	10^7	50–75	23.8		24.8	
7	Bulk single crystal random	0	0	0	10^7	0	31.5	1.6	28.5	1.0
7a	Thermally etched (100)	0	0	0	10^7	50–75	29.9		27.5	

As part of the present series, experiments were repeated on two selected crystals close to the [111] and [100] poles and these confirmed the earlier results. These crystals and some of those used previously (*14*) were examined by electron microscopy.

Structure of the Catalysts

Films on mica. All films were {111}-oriented single crystals. Before catalysis the surfaces of both thick and thin films contained plateaus [ref. (*1*), Fig. 8] which smoothed out rapidly during the initial rate measurements and, after catalysis, the surfaces were quite smooth with grooves along the noncoherent twin boundaries [ref. (*1*), Fig. 10]. When twins were removed by annealing, the surfaces became even smoother and replicas failed to show any features.

Films of each thickness contained the same types of defects, but the concentrations in the thick films were lower by an order of magnitude, and the noncoherent twin boundaries were not removed on annealing. More than 90% of the dislocations in both thin and thick films had a Burgers vector parallel to the (111) plane of the surface.

Films on rocksalt. The films were usually {100}-oriented single crystals [Fig. 1(c)], but sometimes they contained small areas of {111} orientation. Before catalysis, the surfaces of these films appeared rough in the electron microscope [Fig. 1(a)], but during catalysis they became smooth [Fig. 1(b)] and traces of stacking faults or thin twins [Fig. 1(c)] became sharp and distinct. The twins may expose a surface of orientation different from that of the matrix and consequently somewhat less than 100% of the exposed film surface was parallel to (100). In contrast to the stable behavior of {111} films, the {100} films frequently broke up during prolonged catalysis, by the development of polygonal holes with edges in <110> directions. Any {111} grains remained whole and smooth.

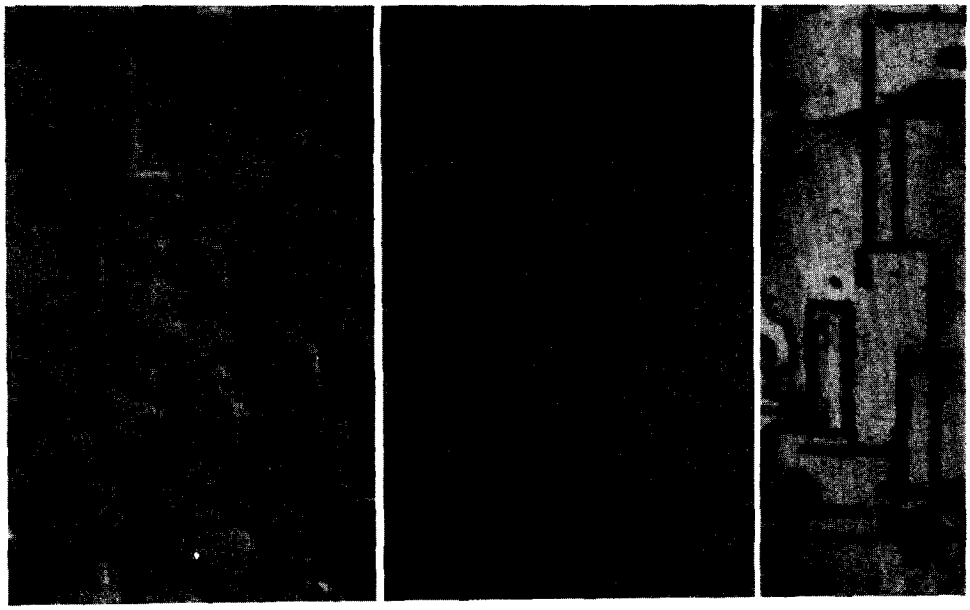

FIG. 1. Electron micrographs of {100} films deposited on rocksalt. 22 000×. (a) and (b) Replicas of surface before and after catalysis, respectively. (c) Transmission through film after catalysis, showing stacking faults or twins.

An example of crystal defects in {100} films is shown in Fig. 2(a). These films have no twinning plane parallel to the surface and therefore noncoherent twin boundaries were absent. The concentrations of dislocations and stacking faults were higher than in {111} films. During catalysis

some of the defects in {100} films annealed out and subsequent heating at 400°C further reduced the concentrations.

Bulk single crystals. Replicas showed that the surfaces of the polished and sputtered crystals [Fig. 3(a)] were smooth but slightly undulating, without any distinct features. No differences between crystals of different orientation and between surfaces before and after catalysis could be detected from replicas.

When the crystals were thermally etched, the surfaces developed ridges [Fig. 3(b)], formed by the intersection of low index and complex facets (*15*). The low index facets were either (111) or (100), depending upon the orientation of the crystals, and the complex facets had high indices. The appearance of the low index facets was unchanged by catalysis but their edges became rounded.

Defects intersecting the surfaces of the bulk single crystals were mostly dislocations. The crystals were thinned from 0.1 cm to about 1000 Å for transmission electron microscopy and this may alter the dislocation structure (*16*). The values of dislocation concentrations so obtained, 10^7–10^9 cm^{-2}, are rather low for this technique to be reliable, but they are in agreement with those obtained by Levinstein and Robinson (*7*), who used the Lambot X-ray technique to study dislocations in silver single crystals grown from the melt.

Electron microscopy and diffraction on thinned and sputtered crystals confirmed that the surfaces were clean and not disorientated by the sputtering (*17*). However, the sputtering introduced voids below the surface [Fig. 2(b)]; presumably they contained argon which penetrated into the crystals and subsequently precipitated. By treating electron microscope specimens with formic acid under the conditions of catalysis, it was found that the voids were quite stable and therefore should not influence the catalytic properties of the surface.

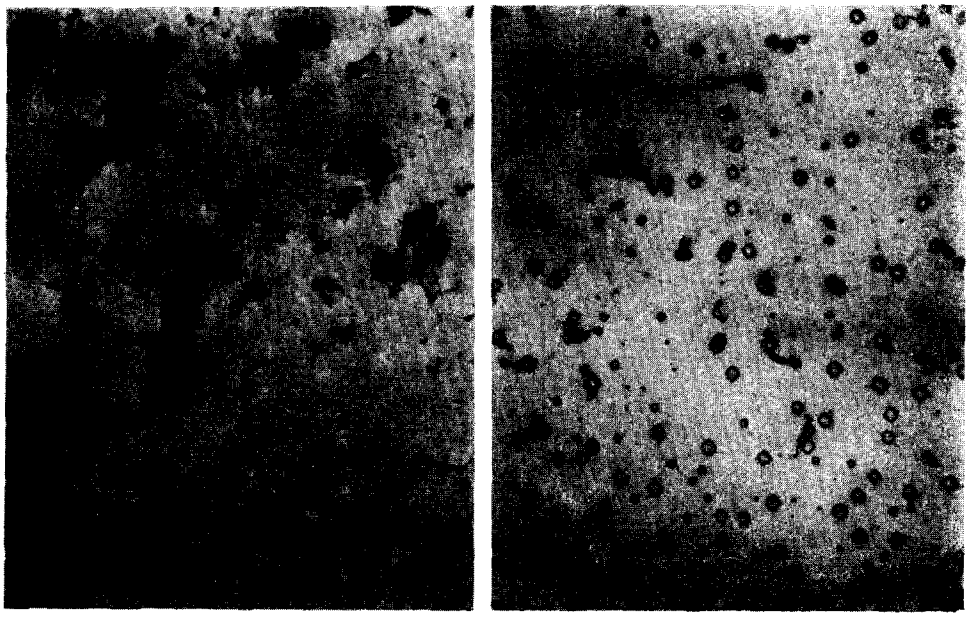

FIG. 2. Transmission electron micrographs. 40 000×. (a) {100} film after catalysis, showing dislocations and short stacking faults (200 reflection). (b) Polished and sputtered bulk single crystal with orientation close to [100], showing voids below surface and a few dislocations (200 reflection).

DISCUSSION

The data in Table 2 show that, in the zero order range, changes in the values of E and A are associated with changes in the surface structure of the catalysts and that therefore the reaction rate is controlled by a surface process which is sensitive to

the structure. The changes in activity can be explained if it is assumed that the surfaces expose active sites with different activation energies, E_i. The compensation effect can then be caused either by variations in concentrations of the different types of active centers, or by differences in activation entropy, or by a combination of both. In principle, E_i and A_i cannot be separately determined from the experimental E and A without knowing the distribution functions. However, by observing how E and A change with surface structure, one can obtain information about the nature of the active centers and thus about their distribution.

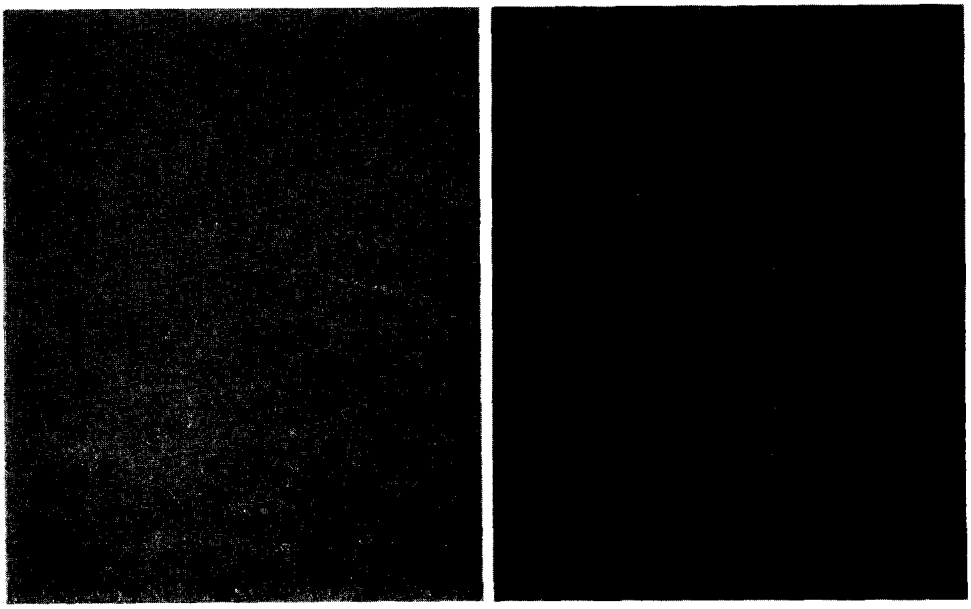

FIG. 3. Replicas of bulk single crystals. 10 000×. (a) Polished and sputtered surface after catalysis. (b) Thermally etched surface before catalysis.

We will first consider the influence of crystal defects, and then separately the reasons for E and A changing with orientation and surface topography.

Crystal Defects

Grain boundaries. These had no influence on the reaction. The values in rows 3 and 4 of Table 2 show that unannealed films of {100} and ({100} + {111}) orientation gave the same values of E and A, although they differed in total length of grain boundaries. The same conclusion was reached previously for polycrystalline films on glass and mica (*1*), and also by other workers for bulk specimens (*18*, *19*).

Stacking faults, coherent twin boundaries, and noncoherent twin boundaries. The influence of these defects on the reaction rate can be determined on surfaces of the same orientation and topography by comparing thin and thick unannealed {111} films (rows 1 and 2 of Table 2) where their concentrations differed by an order of magnitude but the values of E and A were about the same. On annealing, the concentrations of stacking faults and coherent twin boundaries remained unchanged, but the noncoherent twin boundaries were removed in the thin {111} films. However, annealing lowered E and A equally for films of both thicknesses (rows 1a and 2a of Table 2). Also, annealing reduced the concentrations of stacking faults and coherent twin boundaries in {100} films (rows 3 and 3a of Table 2) without influencing the activity.

It is therefore concluded that neither the line defects in the surface, nor the partial dislocations associated with these defects,

influence the reaction. Previously, noncoherent twin boundaries appeared to have an influence (*1*), but it was suggested that this might be caused by the proportion of the (111) area in the surface increasing when these boundaries were removed; the present results support that explanation.

Whole dislocations. In the previous work on evaporated films (*1*), the dislocation concentrations were the same whenever they could be measured, and their influence on the reaction could not be determined. However, Uhara *et al.* (*4*) observed recently that the rate of decomposition of formic acid at a given temperature decreased after annealing specimens which had been deformed by cold-rolling. They concluded that surface terminations of dislocations are active sites for this reaction on silver. In an earlier investigation, Sosnovsky (*3*) had equated differences in A to expected changes in dislocation concentrations in single crystals which had been sputtered at a low temperature, and had come to the same conclusion. An interaction between dislocations was assumed in order to explain why E increased with dislocation concentration, but an orientation dependence of the reaction was not explained, even though it was equally marked. However, in these investigations the dislocation concentrations were not measured and the topography of the surface was not investigated.

In the present work, by comparing thin and thick {111}-oriented films with the same topography (rows 1 and 2, or 1a and 2a of Table 2), it is found that E and A are not altered when the dislocation concentration is changed by a factor of approximately 10^2 both in annealed and unannealed films. Also in {100} films annealing reduced the dislocation concentration but did not affect the activity (rows 3 and 3a of Table 2).

Dislocations could possibly influence a surface reaction in two different ways, either specifically through the properties associated with the point of emergence of the dislocation in the surface or through the action of surface steps, which may be produced by the dislocations.

A high proportion of the dislocations in the {111} films had a Burgers vector parallel to the plane of the surface, and therefore would not create steps on this surface, but they could create kinks in existing surface steps. In a surface already containing a high concentration of natural steps, one would not expect to detect any influence from the steps associated with dislocations, but an effect might have been expected when the surfaces were nearly atomically smooth.

Thus the values show that the points of emergence of dislocations are not active sites for the decomposition of formic acid on silver. Furthermore, surface steps associated with dislocations had no measurable influence.

Orientation and Topography

An influence of orientation and topography was observed on all surfaces. On films, E and A were lowered only when the proportion of (111) planes in the surface increased. Sputtered surfaces of bulk single crystals exposing no detectable (111) or (110) planes gave the highest value of E (31.5 kcal/mole), which decreased by 8 and 2 kcal/mole when (111) or (100) facets, respectively, were produced by thermal etching (rows 6 and 6a, 7, and 7a of Table 2).

All the surfaces were smooth and the influence of orientation can therefore be discussed in terms of atomically flat areas, for which the geometric arrangement of atoms has been calculated (*20, 21*). Figure 4 shows a model of a surface containing (111) and (100) planes and, as an example for the complex facets, the (531) plane. All atoms in (111) and (100) planes have nine or eight neighbors, respectively, and when the orientation moves away from these poles there is an increasing number of monatomic ledges on the surface in which the outer atoms have six or seven neighbors. When the orientation is that of the complex facets (*15*) most of the outer atoms have six or seven neighbors and there are no atoms present with nine and only a few with eight neighbors. For the purpose of the present discussion, such sur-

faces will be called atomically rough and those in which all atoms have the same number of neighbors, atomically smooth.

The changes in E and A can be consistently explained if one associates specific values of E_i and A_i with particular crystallographic planes. The values for the (111) plane (E_{111} and A_{111}) are then equal to the lowest, and those for an atomically rough plane (E_r and A_r) equal to the highest values of E_i and A_i and the values for the (100) plane (E_{100} and A_{100}) are intermediate.

Estimate of E_{111}, E_{100}, and E_r

The values of E_{111} and A_{111} are expected to be lower than the experimental values obtained on even the smoothest {111} films because the surfaces may contain separated monatomic ledges with activation energy E_r. However, on sputtered crystals with an orientation in the same region as that of the complex plane, the whole surface is expected to be atomically rough. Furthermore, the experimental values found on these surfaces are equal to the highest values reported for silver catalysts of atomically rough orientation [Table 3 (*3*, *19*)] and for very finely divided silver catalysts (*22*). Therefore, it should be valid to set E_r and A_r equal to the experimental values obtained on these surfaces, i.e., $E_r = 31.5$ kcal/mole and $\log A_r = 28.5$.

One can then obtain an estimate of E_{111} from the values measured on the composite surfaces of thermally etched crystals containing (111) facets. The low index facets have been shown to be nearly atomically flat (*11*) and the complex facets are all atomically rough and contain no E_{111} areas, so that the relative proportions of surface with E_{111} and E_r can be estimated reliably from replicas. The experimental rate on such a surface is given by a relationship of the following form:

$$\rho = \alpha_{111} A_{111} \exp(-E_{111}/RT) + \alpha_r A_r \exp(-E_r/RT)$$

where α_{111} and α_r are the proportions of (111) and complex facets, respectively, in the surface. If in the above expression one

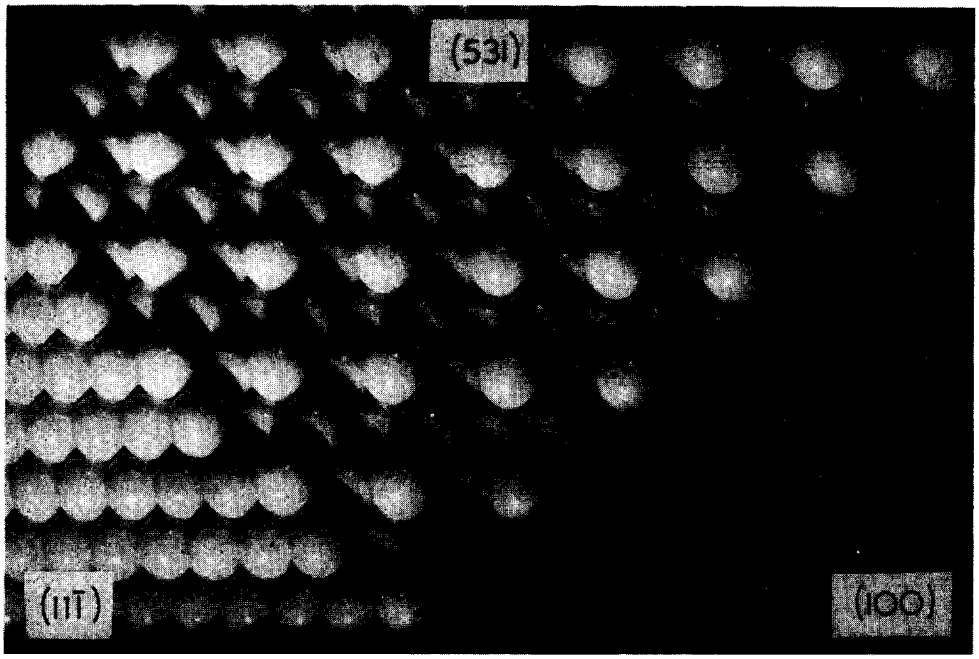

FIG. 4. Model of surface structure on a fcc crystal, showing atomic arrangements of (11$\bar{1}$), (100), and (531) planes. The (531) plane is typical of the complex facets produced on silver by thermal etching.

TABLE 3
ORIENTATION DEPENDENCE OF ACTIVATION ENERGY OF DECOMPOSITION OF FORMIC ACID ON SILVER AND COPPER

	Activation energy (kcal/mole)					
	Ag Zero order				Cu Zero order	Cu First order
		Sosnovsky				
Surface orientation	Jaeger	Untreated	Sputtered argon 15 eV	3000 eV	Rienäcker, Völter Polished	Crocker, Robertson Polished H_2 anneal
(111)	16–17	16	12	23	23.8	19
(100)	24	26	30	35	23.8	8.5
(110)	—	30.4	24	30	—	16
Polycryst.	27	25.5	—	—	23.5	—
Atomic. rough	31.5	—	—	—	—	—

selects values for E_{111} which are lower than E for annealed {111} films, and obtains the corresponding values for A_{111} from an extrapolation of the plot of log A versus E, one can choose the value of E_{111} which is consistent with the experimental rates and the proportions of (111) and complex facets in the surface. This gives 16–17 kcal/mole for the value of E_{111}. Any value lower than this would introduce a noticeable curvature into the Arrhenius plot.

The same procedure can be applied to the {100} films, and if these have about the same atomic flatness as the {111} films, then E_{100} is about 24 kcal/mole.

The activation energies found here are in the same range as the values reported by other workers on silver (*1*, *3*, *19*, *22–25*), and agree with those of Sosnovsky (*19*) for untreated silver single crystals of different orientation given in Table 3. The value of 30.4 kcal/mole reported by Sosnovsky for orientations near [110] may be compared with 31.5 kcal/mole on atomically rough sputtered surfaces of the same orientation measured in the present work. However, in Sosnovsky's work on low-temperature-sputtered crystals (*3*), the activation energies of the (110) crystal were all lower than those of the (100) crystal.

Using these estimates for E_{111} and E_r and the experimental E values for different catalysts, the proportion of (111) planes in their surfaces can be calculated and compared with values obtained from replicas (Table 4). The data indicate that the {111} films contained a greater concentration of surface steps than was judged from shadowed replicas. This difference is due to the limit of resolution of shadowed replicas and is in agreement with the observation that gold evaporated onto these surfaces grows as a continuous sheet. However, the polycrystalline films contained a much larger proportion of (111) area. In this case only the very large grains could be identified in replicas as (111) and the estimate of flat (111) is a lower limit.

The orientation dependence of the activation energy, viz., $E_{111} < E_{100} < E_r$, can be understood from the chemical nature of the unstable reaction intermediate. The detailed mechanism of the reaction is still uncertain, but catalytic measurements combined with infrared studies have been interpreted as identifying chemisorbed formate ions which take part in the reaction on metals (*26*, *27*), and attempts have been made to relate the catalytic activity of different metals to the stability of the bulk formates, i.e., to the strength of the metal formate bond (*27*). However, silver formate is highly unstable (*30*) and a surface formate is expected to form without removing metal atoms from the crystal lattice.

The activation energy measured in the present work represents the energy which the chemisorbed species must acquire to become activated for decomposition. If one assumes that the activated complex is the

TABLE 4
COMPARISON OF CALCULATED PROPORTION OF (111) PLANES IN THE SURFACE WITH ESTIMATES FROM SHADOWED REPLICAS

Catalyst	Surface	E_{exptl} (kcal/mole)	Proportion of (111) Planes in the surface (%)		
			Calculated with E_{111} (in kcal/mole)		Estimated from replicas
			16	17	
{111} films	Annealed	20.8	80	86	95
10000 Å	Unannealed	25.8	47	52	80
Bulk single crystals	(111) facets thermal etching	23.8	64	68	50–75
Films on glass	Polycrystal	27.1	41	45	8–15

same for all orientations, then the differences in activation energy are related to the varying strength of the chemisorption bond and thus to the coordination of the metal atoms in the surface. For example, atoms at the top of ledges, having few neighbors, could form strong formate bonds and if this species is involved in the reaction a high activation energy is required for decomposition; but atoms in (111) planes have few free bonds available, so that the formate bond is expected to be weak and the activation energy would be low. One can thus consider the outer atoms in the surface as active sites for the reaction. Then E_{111} and E_{100} are associated with atoms having nine or eight neighbors, respectively, and E_r is associated with surfaces containing high concentrations of atoms with seven or six neighbors and small concentrations of atoms with eight neighbors.

However, dissociative chemisorption not only makes use of the free bonds of atoms in the surface but leads to the breaking of metal–metal bonds if the formate is stable (*28*). Then metal atoms are completely removed from the metal lattice even at moderate temperatures (*29*), and the activation energy in the zero order range should be independent of orientation. This is consistent with the results obtained by Rienäcker and Völter (*18*) on copper single crystals (Table 3).

If it is correct that the activated state is the same for all decomposing molecules, then the differences in activation energy should reflect changes in the heat of chemisorption of formic acid, which is expected to be higher on atomically rough facets than on (111) planes. No measurements of the orientation dependence of the heat of adsorption during reaction have been reported, but an indication of the trend can be obtained from the data in Table 3. In the first order range, where the measured activation energy is that of the chemisorption process (*31*), Crocker and Robertson (*32*) found for copper an orientation dependence opposite to that in the zero order range for silver measured in the present work. This is expected, since the activation energy of chemisorption is usually found to increase with decreasing heat of chemisorption.

In this model, not all metal atoms which could be potentially active sites for the reaction are active, because the concentration of the chemisorbed species during reaction depends on the stability of the formate. Tamaru has shown that the coverage during reaction is about one adsorbed formic acid molecule to about ten surface atoms on silver (*22*) but to one on copper (*33*). As yet, no measurements of the orientation dependence of coverage during reaction have been reported, but if the compensation effect in the present work is caused by differences in entropy of activation, then the coverage would be about the same for all orientations. In terms of the suggested model, the differences in A for the reaction would then reflect the differences in entropy of the chemisorbed species. Weak binding such as on E_{111} sites produces a low activation energy, but the

probability of reaction is also low, because greater rearrangements are necessary to change the chemisorbed species into the activated configuration. If it is assumed that the formate ion decomposes by a unimolecular process, then the value of log A (28.5) on the atomically rough surfaces is in good agreement with the value expected from absolute rate theory (*34*). This suggests that here the entropy of activation is zero and the difference of 7 in log A between this surface and a (111) plane is equal in magnitude to the difference expected if the entropy changed from that of immobile to mobile adsorption with completely preserved rotation (34 e.u.). It is possible, however, that the reaction is bimolecular on silver (*26*), and a better understanding of the reaction mechanism is required before values of the pre-exponential factor can be interpreted reliably.

Conclusions

The catalytic activity of both films and crystals depended upon the surface orientation, but did not change when the concentrations of crystal defects were altered.

It is suggested that metal atoms are the sites for the reaction and that A and E increase with the number of free bonds of the metal atoms in the surface.

Because (111) and (100) are singular surfaces containing only atoms with three or four free bonds, respectively, one can estimate the values of E associated with them.

It is difficult to extend this analysis to other flat surfaces because they contain atoms with more than four free bonds together with atoms having less than three free bonds. However, the latter might not be accessible to the formic acid because they are partly buried in the surface. If this is correct, one could in principle determine values of E associated with atoms having five free bonds on (110) and (311) surfaces and check the assumption.

The values observed in the present work indicate that E on the atomically rough surfaces was mainly determined by atoms with five and six free bonds.

The results point to the need for more direct information about the number of steps on smooth surfaces of metal catalysts.

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