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### Title

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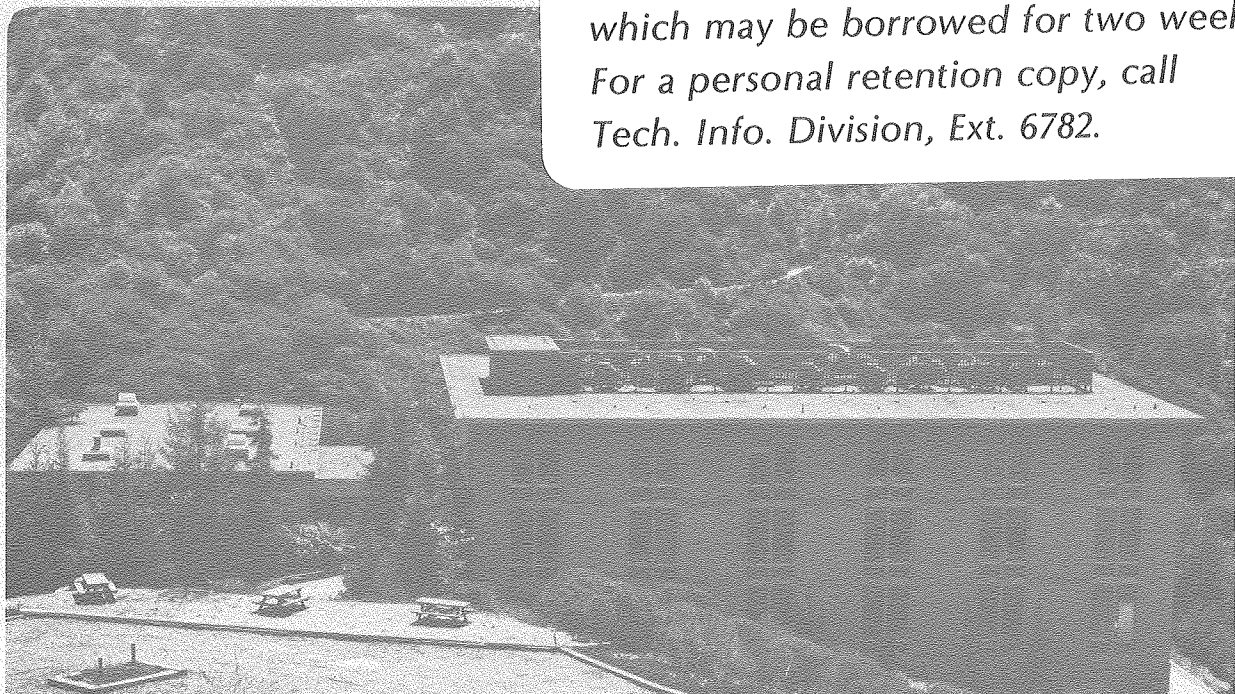
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R.G. Carr and G.A. Somorjai

August 1980

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HYDROGEN PRODUCTION FROM PHOTOLYSIS OF  
STEAM ADSORBED ONTO PLATINIZED SrTiO<sub>3</sub>

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Photodissociation of high pressure (1-8 atm) water vapor adsorbed onto the partially platinized surface of single crystal SrTiO<sub>3</sub> has been observed. The reaction is catalytic; several thousands of monolayers of hydrogen have been produced. The reaction requires light of greater than bandgap (3.1 eV) energy, and proceeds vigorously only if elevated temperatures (375-450 K) and high pressures are used. Recombination of products and poisoning of the metal appears to diminish the reaction rate after several hours. This reaction differs from the photolysis of water in the analogous short-circuit electrochemical cell in that we use no electrolyte and we are able to use non-conducting, stoichiometric SrTiO<sub>3</sub> because bulk electrical conductivity has little influence on localized surface reactions.

A reaction chamber made of stainless steel was fitted with a sapphire window and placed in the oven of a gas chromatograph. Light from a high pressure mercury discharge lamp passed through the window and was incident on the surface of the crystal. The intensity was about  $10^{16}$  photons/cm<sup>2</sup>-sec. in the energy range above the band gap. A single crystal wafer of SrTiO<sub>3</sub> with nominal (111) orientation was rough-polished and coated in vacuo with platinum evaporated from a tungsten filament. The roughness of the surface ensured that it was only partially covered with platinum. The photo-reaction rate was highest with a transparent coating of platinum and decreased with heavier, more opaque coatings, which would cover all semiconductor surface sites.

Ultrapure water was admitted into the evacuated cell at the beginning of an experiment, and pumped through a loop which included the cell and an

automatic sampling valve, so that gas samples could be withdrawn periodically. A sample was then analyzed in the gas chromatograph which was fitted with a thermal conductivity detector. With argon carrier gas, we could detect 10 monolayers of  $H_2$  easily, and  $O_2$  with about 20 times less sensitivity. The whole system accessible to water vapor was kept at uniform temperature so that high pressures could be achieved. Figure 1 shows the cell design.

Figure 2 shows  $H_2$  accumulation curves as a function of time for different temperatures, where the saturation vapor pressure of water was used in each case. In order to inhibit the recombination of  $H_2$  and  $O_2$  products, a few grams of 1 mil Cu foil was placed in the reaction cell to getter the  $O_2$  present. Without this extra copper to oxidize, and thus remove active  $O_2$  from the system, less than half the  $H_2$  would be detected. Oxidation of Cu by water with a release of  $H_2$  was ruled out by blank experiments. Thus the recombination of hydrogen and oxygen is a significant process under these conditions. This is not surprising in view of the presence of platinum and a light activated semiconductor, either of which might act as a catalyst. Because of this back reaction,  $O_2$  was not detected. Blank experiments showed no hydrogen production without platinum on the crystal, nor with platinum on an alumina substrate, and very poor production when platinum was deposited on the dark side of the crystal.

The curves in Figure 2 show an induction period which depends on exposure to water vapor. If the crystal is exposed to water vapor in the dark for one to two hours, hydrogen production will proceed immediately upon illumination. However, when the crystal is illuminated in vacuo for the same period and then exposed to water vapor, the induction period is observed. Thus there is evidence for a slow surface reaction, such as hydroxylation or displacement, which appears to be a necessary precursor for the efficient catalytic photolysis of water observed after the induction period. During efficient hydrogen production, a rate of as much as 500 monolayers per hour has been observed. Within about 10 hours, however, the hydrogen production rate diminishes. Besides equilibration of the production and recombination rates there is also a surface poisoning effect which contributes to this decline. If a crystal used in the experiment is not regenerated by replacement of the platinum coating, it will yield much less hydrogen in a subsequent experiment. A similar deactivation was noted by Wrighton et al.<sup>1</sup> in the  $SrTiO_3$ -Pt electrochemical cell.

It was possible to carry out the photolysis of water at less than saturation vapor pressure. At constant pressure, the reaction rate declines with increasing temperature, as expected, since the recombination over platinum is more facile at higher temperatures. At constant temperature, the rate of hydrogen production increases with increasing pressure.

Recently we reported the photocatalyzed dissociation of water vapor on platinum coated and metal-free  $\text{SrTiO}_3$  crystal surfaces which were covered with a film of NaOH.<sup>2,3</sup> The need for NaOH was traced to the importance of hydroxylation of the oxide surface. Under the conditions of the present experiment the surface is expected to be hydroxylated,<sup>4</sup> and this effect is apparently equivalent functionally to the effect of NaOH.

In conclusion, we have observed evidence for the following steps during photolysis of water on platinized  $\text{SrTiO}_3$ : (1) generation of electron-hole pairs by light of greater than bandgap energy, (2) dissociative chemisorption of water vapor on the hydroxylated semiconductor surface, (3) diffusion of a surface hydrogen species to platinum islands and desorption of hydrogen from the islands, and (4) recombination of hydrogen and oxygen which limits the amount of hydrogen that can be generated in a batch reactor.

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#### References

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Figure Captions

Figure 1. Apparatus: (a) stainless steel cell, (b) U.V. light from Hg lamp, (c) sapphire window, (d) SrTiO<sub>3</sub> crystal with Pt on the side facing the light. Water vapor circulates through cell, pump, and sampling valve.

Figure 2. H<sub>2</sub> product accumulation for four different temperatures at H<sub>2</sub>O saturation vapor pressures.

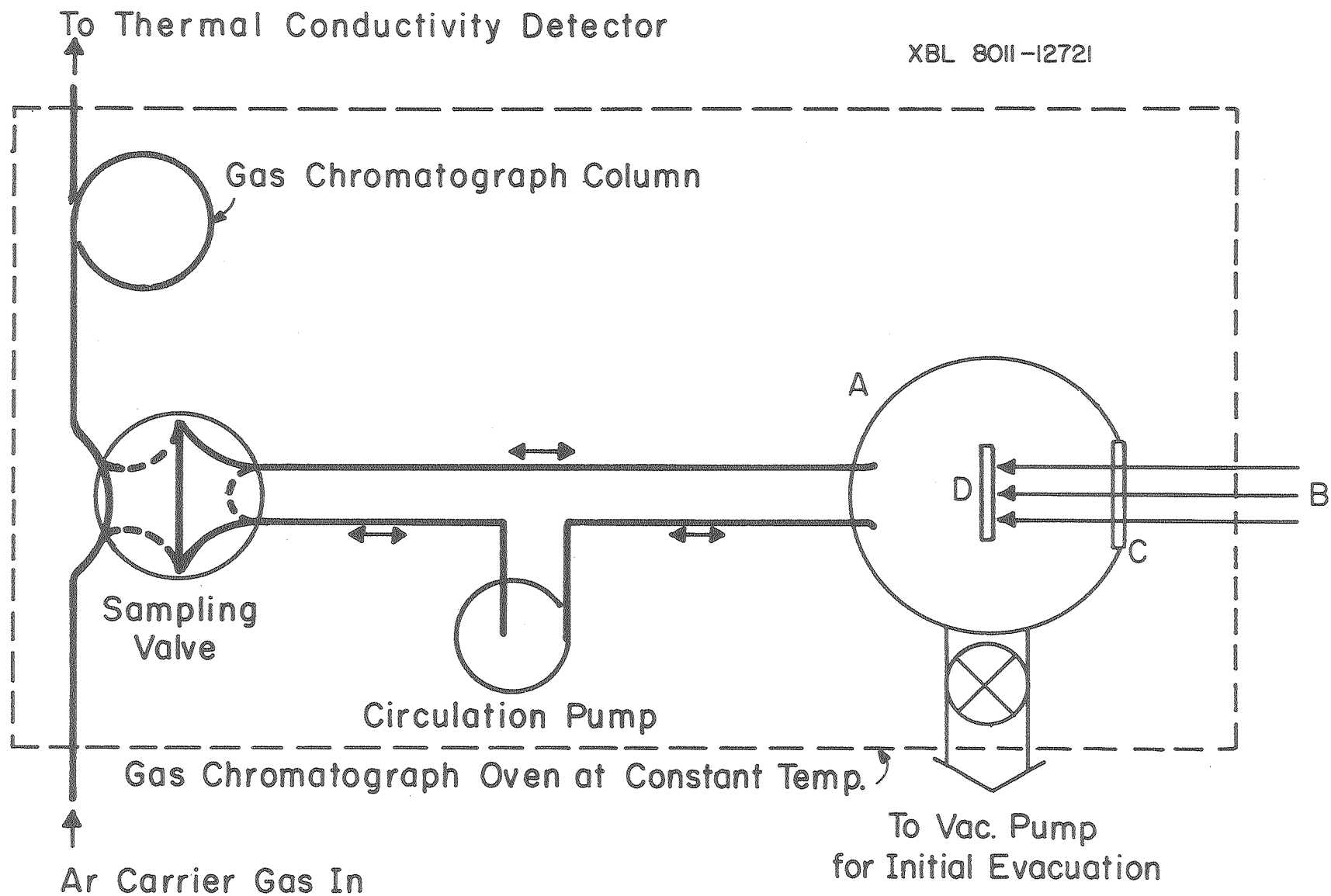


Fig.1



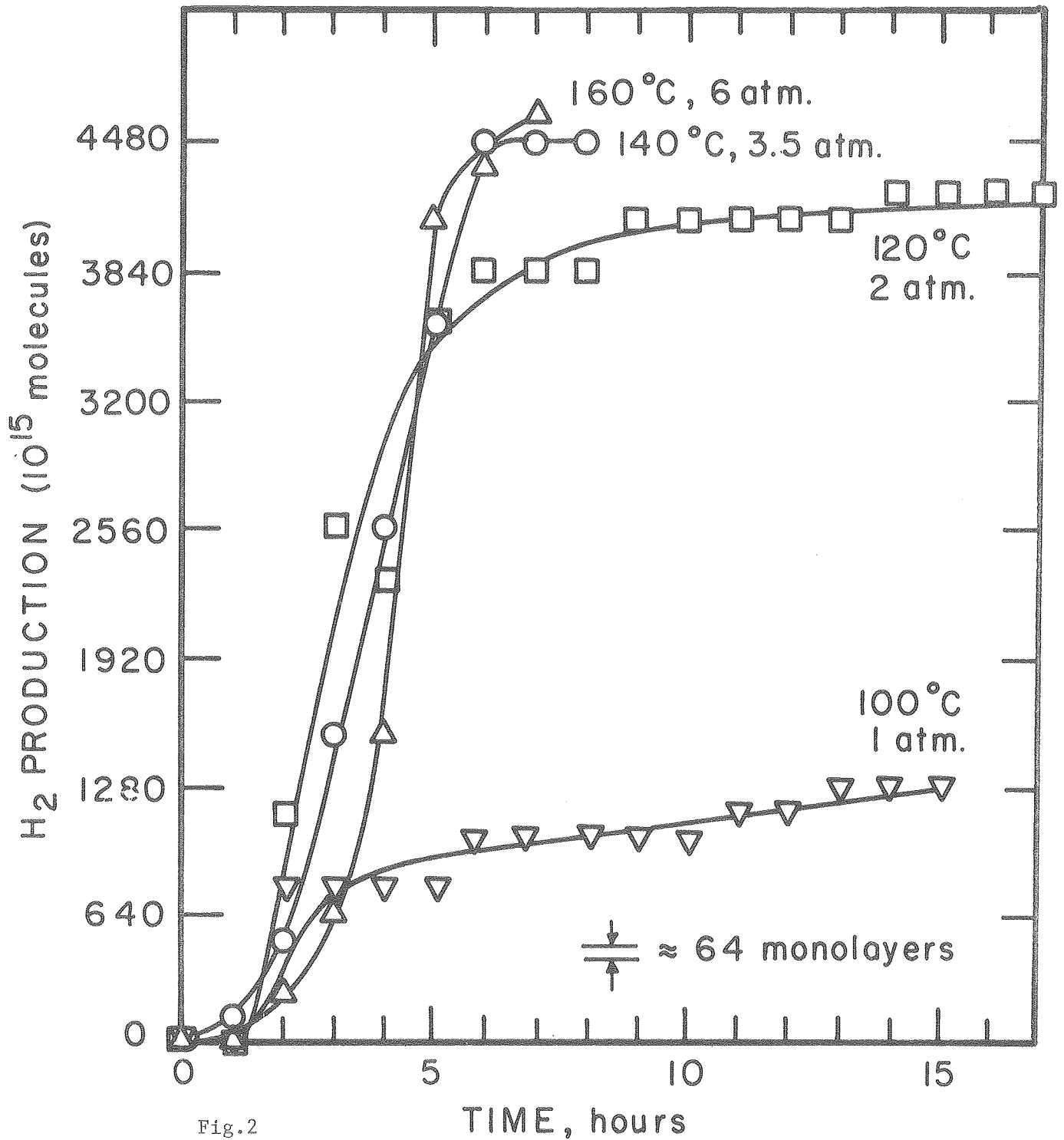


Fig.2

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