

HYDROGEN DIFFUSION IN WO_3 THIN FILMS

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ABSTRACT

The diffusivity of electrolytically introduced H in WO_3 thin layers was measured optically using a 1 μm resolution power microdensitometer. The diffusion coefficient was found to decrease with increasing H content. The observations were described by a modified percolation model.

Hydrogen diffusion in solid phase is thought to be one of the rate determining factors in the electrochromatic processes of WO_3 . Earlier the determination of the diffusion coefficient was tackled by the NMR technique (ref.1) and through chronoamperometry (ref.2), the first method resulted in an order-of-magnitude estimate whereas the second one offered indirect information only. The aim of the present work was the direct experimental determination of the diffusivity of H in WO_3 .

In order to measure lateral diffusion part of a thin WO_3 film on an SnO_2 /glass substrate was covered with an insulating photoresist layer then the wafer was immersed in acid solution to saturate the uncovered portion with H under potentiostatic conditions. Indicated by blue coloration a H concentration profile was formed which was homogeneous in depth and width and showed the shape of a step function perpendicular to the edge of the insulating layer. The spread of this profile was measured optically by making use of a microdensitometer. The analysing light was kept as low as possible to avoid photochromatic effect and thermal decomposition. The lateral resolution of the method was about 1 μm , the long time stability of the apparatus in the order of 0.1 %/hour. The typical duration of a run was about 8 hours.

The asymmetric shape of the time dependent lateral concentration distribution, $c(z,t)$, indicated some concentration dependence of the diffusion coefficient, $D(c)$. This suggested the advisability of using Boltzmann's transformation (ref.3). On introducing the new

variable $y=z/\sqrt{t}$ the observed $c(z,t)$ functions were transformed into $c(y)$ which yielded

$$D(c) = \frac{1}{2} \frac{dy}{dc} \int_c^{c_0} y \, dc \quad (1)$$

Having smoothed the $c(y)$ data, $D(c)$ could be calculated by standard numerical differentiation and quadrature computer routines. The results are summarized in Fig.1.

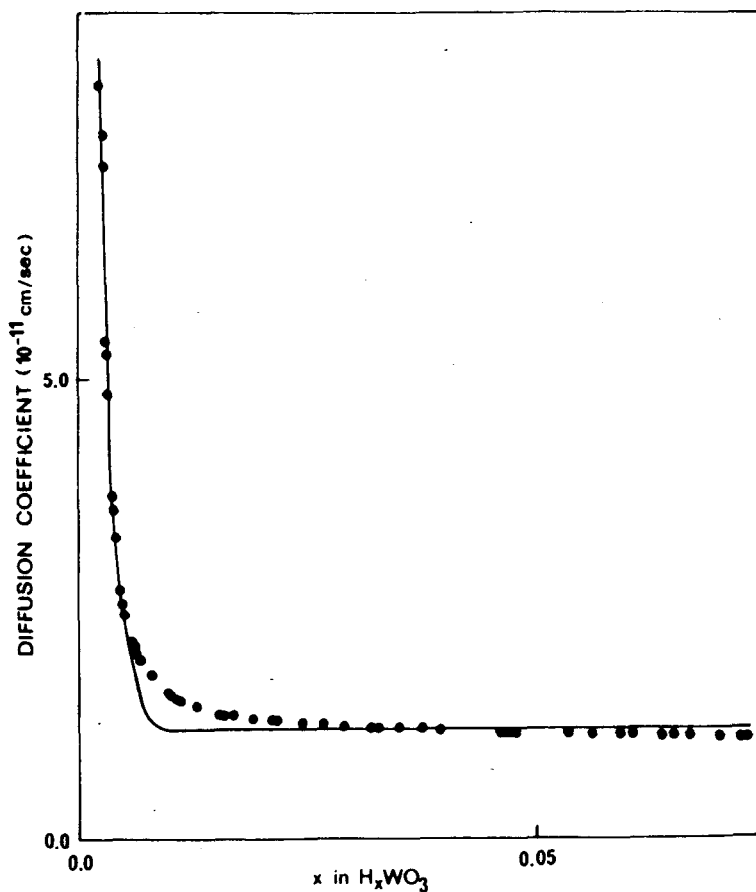


Fig. 1. Diffusion coefficient of H in H_xWO_3 layers as a function of H content

WO_3 is known to have a crystal structure which exhibits two types of channel both of which are perpendicular to the (001) plane. This fact prompted us to attempt the understanding of the concentration dependence of D in terms of two-channel diffusion. It was easy to show, however, that diffusion which proceeds along

two types of independent channels with different diffusion coefficients was an inadequate model to bring out the functional form of $D(c)$ measured by us. Any model of this kind resulted in a minimum curve in sharp contrast with observations. This inadequacy could not be remedied even by assuming that the proportion of the two types of channel depended on c , i.e. that H atoms caused jamming one type of channel.

Abandoning this idea we turned to percolation theory, i.e. to a two-channel diffusion in which slow and fast channels cross each other and fast motion of the diffusant is possible only if at least one infinitely large contiguous cluster of fast channels is present (ref.4). We developed this basic model by making use of the simple assumption that the fraction of fast channels, p , decreases linearly with H content, i.e.

$$p = p_0 - \alpha x \quad (2)$$

Combining this with Landauer's (ref.5) effective medium description of percolation (where p plays a central role), an analytical expression for $D(c)$ was obtained. (There is an obvious proportionality between c and x , the H content of WO_3). Effective medium theory describes D as a function of p by the expression,

$$D(p) = D_0 [b + (b^2 + r/2)^{1/2}] \quad (3)$$

where

$$b = \frac{1}{2} \left[\left(\frac{3}{2} p - \frac{1}{2} \right) (1 - r) + \frac{1}{2} \right]$$

The combination of eqs.(2) and (3) was fitted to the experimental data; the result is given in Fig.1. The agreement seems to be reasonable. The parameters were found to be $D_m = (1.07 \pm 0.31) 10^{-11}$ cm^2/sec ; $D_0 \sim 10^{-9}$ cm^2/sec ; $\alpha = 28 \pm 16$; $p_0 = 0.49 \pm 0.09$. A some two orders of magnitude difference between the diffusion coefficients of H in a virgin WO_3 sample and in an H-containing one is to be seen.

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