

PREPARATION OF AMORPHOUS V_2O_5 THIN FILMS BY CHEMICAL VAPOR DEPOSITION METHOD

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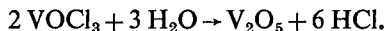
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(Received January 30, 1979)

Amorphous vanadium pentoxide thin films have been prepared by chemical vapor decomposition of $VOCl_3$ with H_2O in inert atmosphere at room temperature. The films crystallize at around $240^\circ C$ irreversibly. The d. c. electrical resistivity in the amorphous state is approximately 1-2 orders of magnitude lower than in the polycrystalline state.

Vanadium pentoxide, V_2O_5 , is known to contain both V^{4+} and V^{5+} ions and the electronic conduction is due to the hopping motion of the unpaired 3d electron from V^{4+} to V^{5+} ions (small polaron hopping). Due to the difficulty of preparing pure vitreous V_2O_5 most of the previous studies on its semiconducting properties were carried out on glasses containing vanadium pentoxide as a component. Until now vacuum deposition [1-3] and splat cooling [4-6] have been successfully applied to prepare amorphous V_2O_5 .

Chemical vapor deposition (CVD) proved to be a convenient method for growing crystalline vanadium oxides [7]. Relatively high reaction temperatures (above $600^\circ C$) are needed to grow single crystals of good quality. Since the decomposition of $VOCl_3$ vapor with H_2O vapor is a strongly exothermic process, the reaction already takes place at room temperature according to the equation:



Based on this reaction the CVD method can be applied to obtain amorphous vanadium pentoxide. In this paper we report the successful preparation of amorphous V_2O_5 thin films by chemical vapor decomposition of $VOCl_3$ with H_2O in inert atmosphere.

The schematic diagram of the apparatus used is shown in Fig. 1. The vapor of $VOCl_3$ (FLUKA; Switzerland) and H_2O thermostated at $22^\circ C$ was led to the reaction chamber by high purity N_2 gas flow. To avoid the chemical reaction of water vapor traces in the $VOCl_3$ containing ampulla, the carrier gas was led through an LN_2 baffle. As substrate material quartz plates (HERASIL I; Germany) were used. The colour of the freshly prepared films varied from yellow to orange depending on the reaction time typically 10 through 20 minutes. The thickness of the films determined by optical method was of some thousand Å.

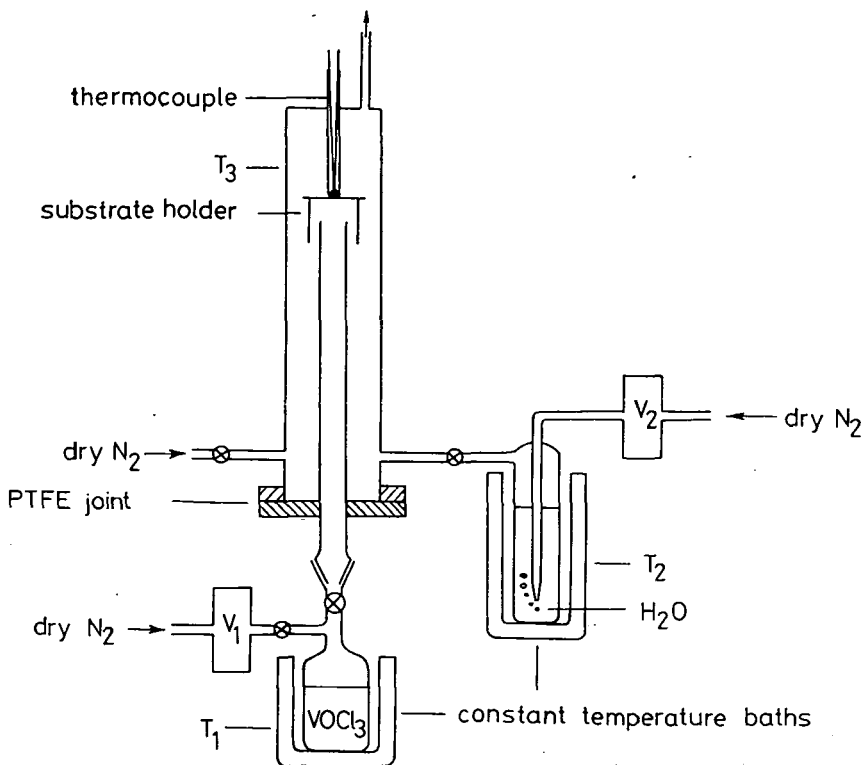


Fig. 1. V_1 , V_2 -flowmeters (Rotameter MFG. Co. Ltd. England) \otimes -PTFE valves (Corning, England) $T_1 = T_2 = T_3 = 22^\circ \text{C}$, $V_1 = 1$ lit/hours, $V_2 = 0.7$ lit/hours

LIVAGE *et al.* pointed out that the solubility of the two phases is extremely different. Crystalline V_2O_5 can not be dissolved in water while the amorphous oxide readily dissolves [5, 6]. Our films prepared by the CVD method easily dissolved in water, yielding strongly acidic solution with $\text{pH} \sim 2$, in accordance with the results of LIVAGE and COLLONGUES. The results of microscopic examination in polarized light and electron diffraction pictures unambiguously verified that these films were amorphous.

The crystallization temperature of the amorphous oxide obtained by splat cooling is between 180 and 200°C [5, 6]. The crystallization is an irreversible, strongly exothermic process. Because the crystallization can be followed by electrical measurements, we studied the temperature dependence of the d.c. electrical resistivity of the amorphous V_2O_5 thin films from room temperature up to 300°C in dry O_2 atmosphere. The platinum electrode were deposited on the substrates by vacuum evaporation before the preparation of the films. Applying a constant heating rate of $0.5^\circ \text{C}/\text{min}$, a decrease in the conductivity could be observed at around 240°C in each case. We found a ratio of 10 – 10^2 between the conductivity of the two phases. The material of the films heated above 240°C was insoluble in water. The

microscopic re-examination in polarized light demonstrated, that the films had been crystallized (Fig. 2).

To determine more precisely the value of the crystallization temperature the influence of the annealing was studied on initially amorphous films. The samples were held for 3 hours at different temperatures: (a) 180° C, (b) 200° C, (c) 220° C, and (d) 240° C. The resistivity of the samples was steadily measured during this annealing process. Samples (a), (b), and (c) exhibited no changes in the resistivity, while the resistivity of sample (d) increased by approximately two orders of magnitude.

The microscopic examination showed that the film when annealed at 240° C crystallized completely.

Summing up we conclude that the chemical vapor decomposition of $VOCl_3$ with H_2O in inert atmosphere at room temperature proved to be a reliable method for preparing amorphous vanadium pentoxide thin films. The films crystallize at around 240° C irreversibly. The d.c. electrical conductivity in the amorphous state is approximately two orders of magnitude higher than in the polycrystalline state.

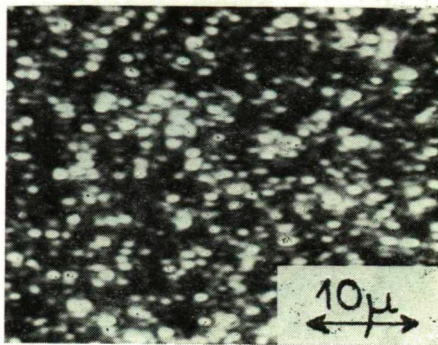


Fig. 2

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ПРИГОТОВЛЕНИЕ АМОРФНЫХ ТОНКИХ СЛОЕВ V_2O_5 МЕТОДОМ РАЗЛОЖЕНИЯ ГАЗОВОЙ ФАЗЫ

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Описано приготовление тонких слоев V_2O_5 путем химического разложения газовой фазы $VOCl_3$ с H_2O в инертном газе при комнатной температуре. Пленки кристаллизуются около 240° C по необратимому пути. Электрическое сопротивление аморфного состояния по постоянному току ниже на 1—2 порядка по сравнению сопротивлением поликристаллического состояния.