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Gas Sensitive Behaviour and Morphology of Reactive Evaporated V_2O_5 Thin Films

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The gas-sensing characteristics and the morphology of vanadium pentoxide thin films have been investigated. The thin films were prepared by reactive electron beam evaporation of vanadium on surface-oxidised silicon wafers and additional thermal oxidation. Structural and morphological analyses of the V_2O_5 thin films in the thickness range of 100–200nm were performed. The polycrystalline monophase V_2O_5 films consist of grains with surface areas in the range of 100 nm to 1 μm square. Gas measurements were carried out with single-chip thin-film sensor arrays in synthetic air with 50% humidity. The sensors are analytically suitable as they are sensitive to ammonia, methane, carbon monoxide and nitric dioxide. Particularly for NO_2, a distinctive temperature dependence of the gas reaction has been observed.

1. Introduction

Vanadium pentoxide (V_2O_5) is normally a nonstoichiometric material with oxygen vacancies. These vacancies effect n-type semiconducting behaviour. The bandgap is 2.26 eV at room temperature and the donor levels of oxygen vacancies are approximately 0.15–0.17 eV beneath the conduction band edge.[(1)]

V_2O_5 is commonly used in chemical processes as a catalytic activator in oxidation reactions. For example, V_2O_5 is used in the oxidation of SO_2 to SO_3 or to split off Cl_2 from HCL.[2] These commonly known catalytic properties could be, by an expected reduction of activation energies for chemisorption of gas molecules, very useful in promoting high gas sensitivities.

These expectations were in principle recently verified by Schilling and Colbow.[3] They reported on the hydrogen sensitivity of Pt-loaded V_2O_5 thick films. These thick films were prepared by the sintering of V_2O_5 powder (99.5% purity) and by evaporation of V_2O_5 on an Al_2O_3 substrate. One of the drawbacks is that thick film technology is hardly compatible with standard microelectronic technologies, which may be a promising as well as an easily tunable way to develop and produce low-cost semiconductor gas sensors with stable and reliable properties. A review of the literature revealed that to date, thin film gas sensors based on V_2O_5 have not been reported. Thus we decided to investigate the possibility of combining thin film processed V_2O_5 with our standard design for semiconductor chemical gas sensor development[4] and to investigate its response to different target gases.

2. Experimental Details

The used sensor is a single-chip thin-film sensor array with four sensing elements.[5] The array is structured using conventional photolithography, sputtering and evaporation techniques. A Ta/Pt resistance layer (25/200 nm thick) for heating the device to its operating temperature (300° – 500°C) and interdigital electrodes are deposited and structured on standard (silicon/1 μm insulating SiO_2) substrates. Polycrystalline n-type V_2O_5 (70 nm thick) is sputtered onto the electrodes. The deposition was performed by electron beam evaporation of vanadium with oxygen pressure.

3. Results and Discussion

3.1 *Morphology*

The material is as deposited, and is not completely oxidised and still shows metallic conductivity. Therefore, an additional oxidation (1 h) at 500°C in synthetic air was performed in a diffusion furnace. The annealing causes a significant growth of the crystals (Fig. 1). The sheet resistance rises from about 1×10^5 Ω/square to the semiconduction range of 0.5×10^8 Ω/square. The annealed layers stick well to the substrate. Nevertheless, the V_2O_5 was overgrown onto the Ta/Pt interdigital electrodes and onto the SiO_2 surface between the electrodes. They withstand the standard adhesive tape test as well as shock cooling in liquid nitrogen. The morphology and the crystallographic characteristics of the V_2O_5 layer were investigated with X-ray analysis (XRD) and a scanning electron microscope (SEM). The polycrystalline film consists of grains ranging in size from 100 nm to 1 μm square (Fig. 1). The common theta/2theta plot proved the monophase behaviour and indicates a significantly textured growth in the <001> direction for the layer (Fig. 2). For the n-type semiconductor SnO_2 it is known that the gas response differs depending on the morphology. Thus, it is important for a later interpretation of the gas sensor behaviour of

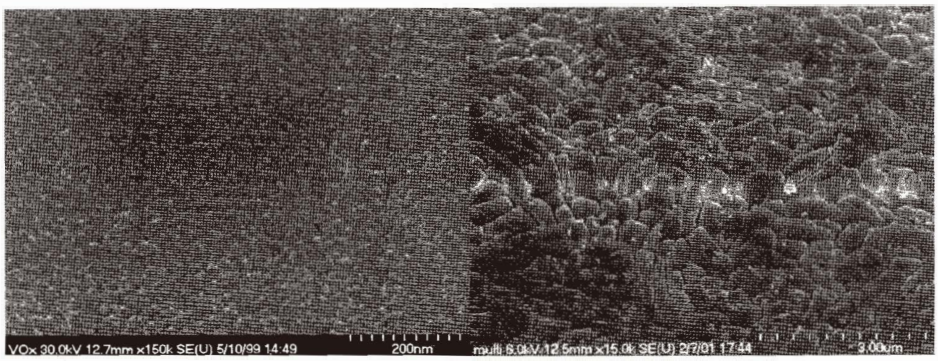

Fig. 1. SEM images of the V_2O_5 layer as grown (left) and after annealing for one hour at 500°C in synthetic air (right). After the annealing process, the surface areas of the crystals are in the range of one micrometer square.

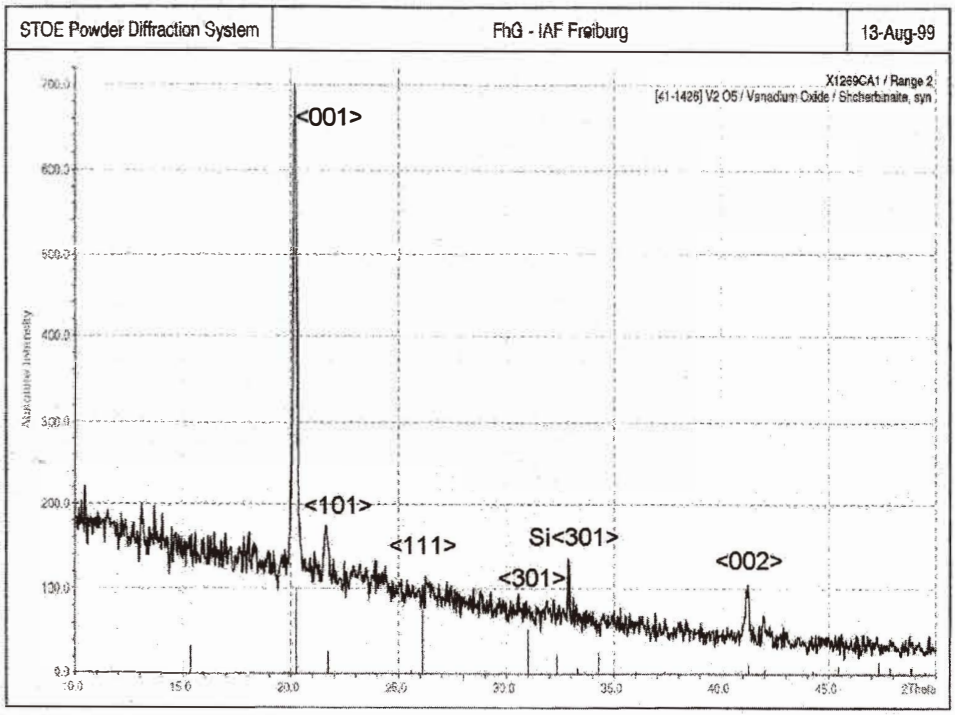

Fig. 2. X-ray-theta/2 theta spectra of the reactive evaporated V_2O_5 thin film layer on SiO_2 / Si-substrate and after annealing for one hour at 500°C in synthetic air. For comparison, peaks and relative X-ray intensities for V_2O_5 [PDF(Powder Diffraction File)-41-1426] are indicated (theoretical intensities:): 100% [20.2°], 75% [26.1°], 52% [31.0°], 27% [21.7°], 11% [41.2°][3.59]).

V_2O_5 to analyse this issue carefully. An additional X-ray pole figure around the intensity maximum for the <001> reflex verifies this significant fibre texture as a further interference pattern is absent. Figure 3 shows the X-ray pole figure around $2\theta = 20.26°$.

3.2 *Gas response*

The response of the V_2O_5 sensors to different concentrations of NO_2, CO and CH_4 was measured for an overview at a constant working temperature of 330°C. Figure 4 shows the typical response to these gases in synthetic air (50% r. h., 25°C).

The V_2O_5 sensors show a suitable response to CO and response to NO_2 about 50 times higher, if the results for 0.5 ppm NO_2 and 50 ppm CO are compared. The response times are in the range of seconds as is the recovery time for CO. For NO_2, the recovery time increases with increasing NO_2 concentration. The response and recovery to CH_4 show a fast signal, but in our opinion, in an unsuitable quantity for a possible application in alarm systems. The V_2O_5 layers decrease in resistance if the material is exposed to traces of reducing gases and increase in the case of oxidising gases. The material shows 'n'-type semiconductor behaviour. The observed gas reaction to the investigated gases is qualita-

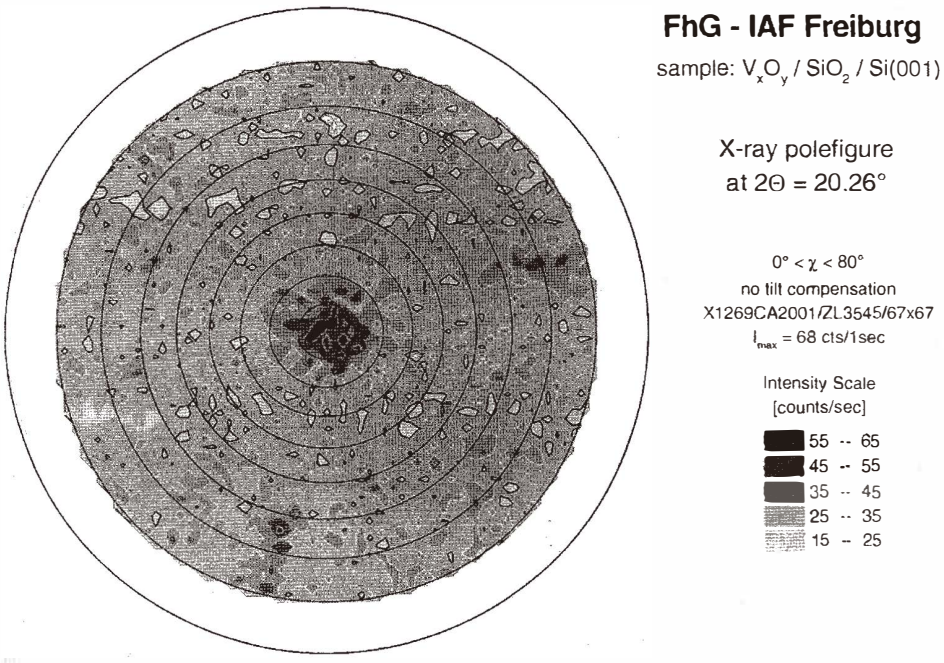

Fig. 3. X-ray pole figure of V_2O_5 around 2θ=20.26°. The pole figure represents the projection of the X-ray-intensities in the plane of a semisphere. The main maximum at 2θ=20.26° is located in the middle of this projection. Each black circle is equal to an increasing angle-increment of 10°. The absence of additional interference patterns (circles) leads to the conclusion of a preferential growth in the <001> direction.

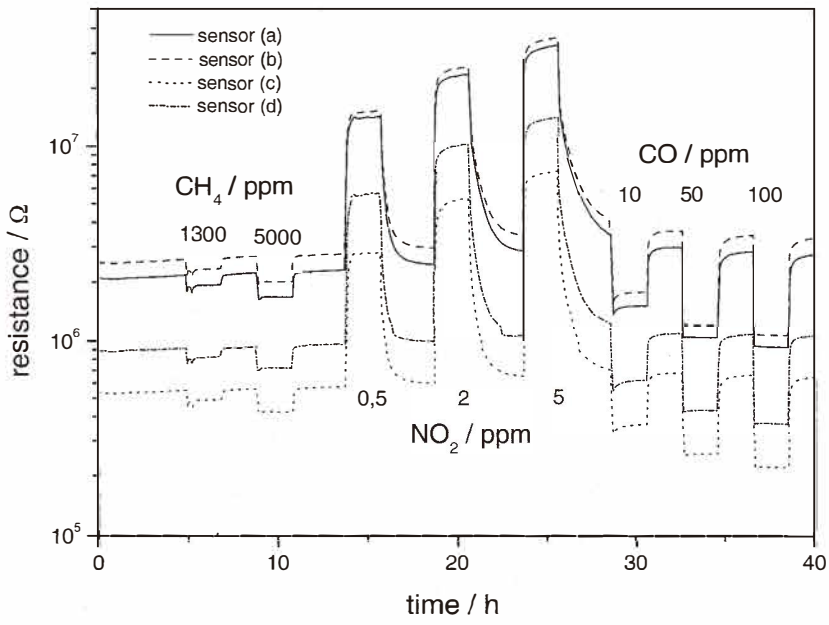

Fig. 4. Response of a V_2O_5 thin film sensor to different concentrations of NO_2, CO and CH_4 in synthetic air at 330°C (50% r.H.). As an insert, the top-view design of the fourfold array layout is shown; the sensing areas and contact electrodes are identical for a), b) and for c), d), respectively. The small differences in the resistances for these identical structures may be due to uncertainties in the adjustment of electrodes and the sensitive layer.

tively similar to that of n-type SnO_2. Figure 5 shows the comparison between CO and NO_2 in more detail in a plot, diagrammed as the response versus the gas concentrations.

Furthermore, the response of these sensors to different concentrations of NH_3 was measured under the same conditions as noted above, as shown in Fig. 6. In the case of NH_3 exposure, the initial response time constants are in the range of minutes. In contrast, the recovery time constants are in the range of hours. Different from the NO_2 reaction, which also shows an extended recovery time (Fig. 4), we observed a varying relaxation behaviour for ammonia (Fig. 6).

Switching off the ammonia flow leads to a fast resistance increase (arrows in Fig. 6) in combination with a slow drift to an equilibrium value. We explain this phenomenon by a superposition of a fast desorption process of the ammonia molecules away from the hot sensitive layer with a slow desorption of NH_3 from the cold surface of our measurement equipment. The sensor follows this slow process immediately and the response directly reflects this memory effect of the chamber. In the case of NO_2, no two-step process was observed.

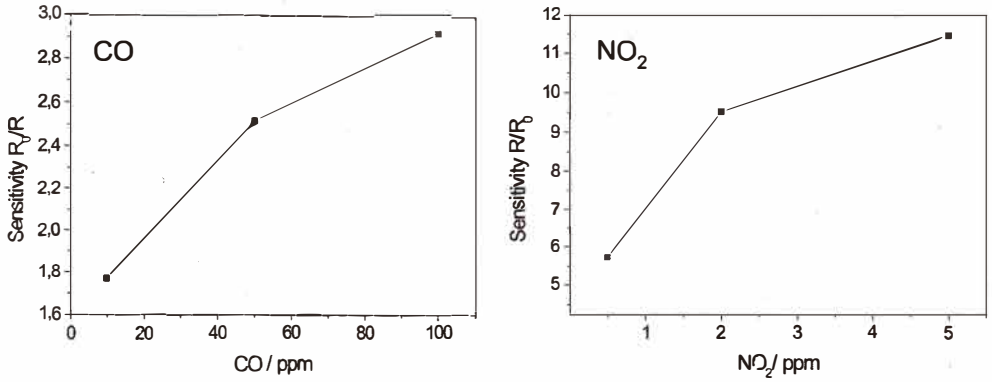

Fig. 5. Comparison of the concentration dependence of the gas response of the thin film V_2O_5 sensor for CO and NO_2. Plotted are the mean sensitivity values R/R_0 determined from the response of 16 sensors. The standard deviation is in the range of 10% from the mean sensitivity values.

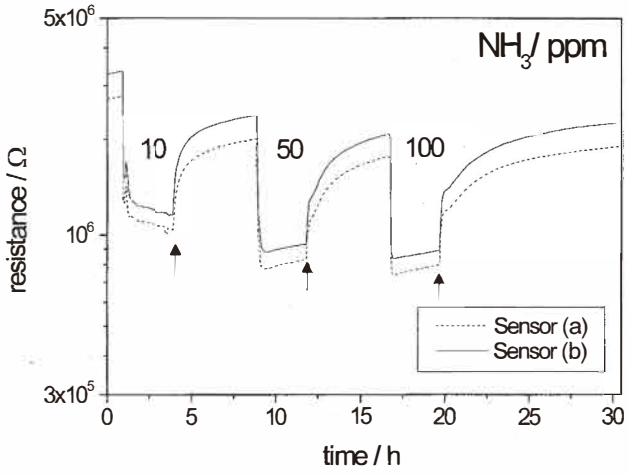

Fig. 6. Response of two V_2O_5 thin film sensing elements of one sensor array to different concentrations of NH_3 in synthetic air at 330°C (50% r.H.).

To characterise the sensing behaviour of this thin film V_2O_5 in more detail, it is necessary to investigate the temperature dependence of the gas response. A set of gas measurements was carried out. In these experiments, the sensor operation temperature was stepped up from 220°C to 390°C. During each 6 h interval in which the working temperature was kept constant, the sensors were exposed for two hours to the investigated

gases. Figure 7 shows the results for 0.5 ppm NO_2 and for 10 ppm CO as a function of working temperature in synthetic air (50% r.H.). The mean sensitivity values R/R_0 determined from the response of 16 sensors are diagrammed. In the analysed temperature range, the NO_2 sensitivity increases strongly with lower temperatures. In the case of CO up to 390°C, no maximum could be found. This was also found for NH_3 and CH_4 (not shown here). As mentioned above for Fig. 4, the gas response is qualitatively similar to SnO_2 as far as the temperature dependence is concerned.[4]

Considering our results, n-V_2O_5 is particularly attractive for the detection of NO_2 at low temperatures. It must be mentioned that, unfortunately, there are some drawbacks to the application of n-V_2O_5. After mid-term exposure (a few days) at temperatures ≥ 400°C, the thin film started to diffuse on the surface. The result is a shrinking accompanied by a drift to higher resistance. In addition, V_2O_5 is known to be less stable against aggressive environments containing acid or alkaline solutions. Furthermore, it has to be taken into account that bulk V_2O_5 is also soluble in water (~0.07g/l).[2]

4. Conclusion

Our experiment results reveal that V_2O_5 thin films significantly react to NO_2, NH_3, CO and CH_4 exposure. At lower temperatures (>270°C) the sensors show an extremely high NO_2- sensitivity.

The observed changes in resistivity of the material under gas exposure reveal n-type conductivity. This means that the conductivity mechanism is governed by oxygen vacancies. In our opinion, the gas sensing mechanism can be described by the common Charge Transfer Model (CTM),[6] because of the similar gas induced response in comparison to that of well known metal oxides such as SnO_2 or WO_3.[7] It is highly probable that as in the case of other semiconducting metal oxides, the morphology of the material strongly influences the gas reaction.[8]

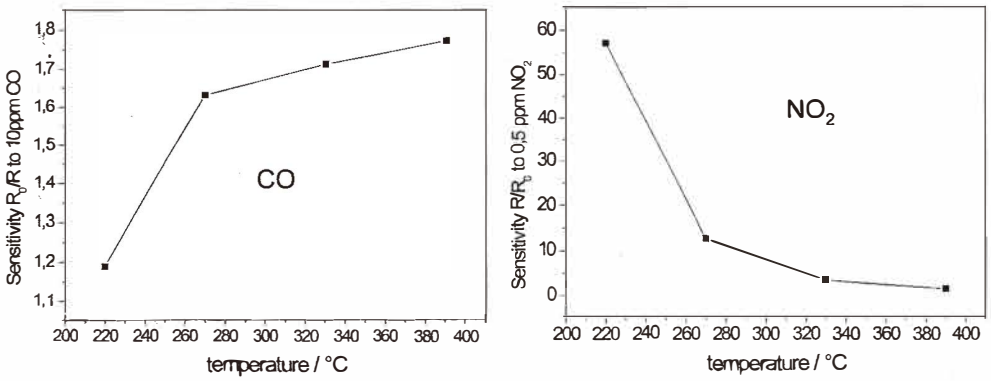

Fig. 7. Temperature dependence of the sensitivity of a V_2O_5 thin film sensor to 0.5 ppm NO_2 and to 10 ppm CO in synthetic air (50% r.H. at 24°C).

The working temperature of the sensors is in the same range as that of sensors based on SnO_2 or WO_3.[7] This behaviour may be a key to the future integration of V_2O_5 sensors together with SnO_2 layers in a single-chip thin-film sensor array, if the restrictions concerning the environment are observed. Here, further investigations are necessary to clarify possible applications for V_2O_5 thin film sensors.

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