# Thermal Oxidation of $V_2S_5$ /InP Heterostructures in Oxygen

I. Ya. Mittova, I. M. Soshnikov, V. A. Terekhov, and V. N. Semenov

Voronezh State University, Universitetskaya pl. 1, Voronezh, 394693 Russia Received March 23, 1999

Abstract—X-ray emission and IR spectroscopy data are used to elucidate the mechanism of thermal oxidation of  $V_2S_5$ /InP structures in oxygen. The substrate–activator interaction is shown to have a significant effect on the oxidation mechanism and to improve the engineering performance of the structures.

#### INTRODUCTION

The application of an oxidation activator directly to the surface of the semiconductor to be oxidized, especially via chemical deposition, gives rise to the formation of active centers at the very beginning of the process. As a result, the oxidation kinetics do not depend on the formation of intermediate species in the gas phase or the competition between these species for the active centers, which may disguise the effect that one of the components of the activator, basically reactive with the components of the semiconductor, has on the oxidation process. Thermal oxidation of activator/semiconductor structures enables one to assess the effects of all activator components, both cationic and anionic, on the kinetics and mechanism of semiconductor surface oxidation and the properties of the resulting structures. Among cation formers, of particular interest are d metals, capable of effectively accelerate oxidation owing to changes in valence state. Sulfur is an attractive anion former, ensuring the same coordination of the substrate components as oxygen.

In this paper, we report our findings on the thermal oxidation of  $V_2S_5/InP$  structures and the composition of the resulting layers.

#### **EXPERIMENTAL**

The activator used was  $V_2S_5$ , having a layered hexagonal structure [1]. Heating in an inert atmosphere at 300–500°C leads to  $V_2S_5$  dissociation,

$$V_2S_5 = V_2S_3 + S_2 - 766$$
 kJ/mol.

As a result, oxidation proceeds in the presence of the two vanadium sulfides and an excess of sulfur. According to Karyakin and Angelov [2],  $V_2S_5$  can be prepared by precipitation from an aqueous solution:

$$2(NH_4)_3VS_4 + 6HCl = V_2S_5 + 6NH_4Cl + 3H_2S.$$

In our experiments,  $V_2S_5$  films were deposited onto polished FIE-1 InP (100) wafers pretreated according

to the following scheme: (1) chemical polishing with a 2 : 1 : 1 mixture of concentrated  $H_2SO_4$ , concentrated  $H_2O_2$ , and water for 10 min; (2) rinsing in bidistilled water; (3) treatment with a chromic mixture to perfect wetting; (4) rinsing in bidistilled water; (5) surface activation for 20 min with a 0.1 M solution of ammonium thiovanadate,  $(NH_4)_3VS_4$ . The substrates thus treated were dipped in a temperature-controlled precipitation bath containing an aqueous solution of  $(NH_4)_3VS_4$  (0.05 M). The precipitant used was hydrochloric acid (pH 8). The solution temperature was maintained at 20°C, and the precipitation time was 6 h. The thickness of the films thus deposited was 70–73 nm.

As-prepared  $V_2S_5$ /InP structures were oxidized in a resistance-heated flow-type quartz reactor at an oxygen flow rate of 40 l/h at temperatures between 400 and 500°C (25°C intervals, ±2°C) for 3 to 60 min. Sulfide and oxide layer thicknesses were determined with an LEF-3M ellipsometer (±1 nm).

### **RESULTS AND DISCUSSION**

The kinetic data were fitted with the Kröger–Ziegler equation [3],

$$x^2 = K \ln \tau, \tag{1}$$

where x is the increase in film thickness (nm),  $\tau$  is the oxidation time (min), and K is the rate constant (nm<sup>2</sup>) (Fig. 1).

Equation (1) provides a good fit to the experimental data, indicating that, as would be expected, the density of active centers in the reaction zone decreases with time.

The apparent activation energy  $E_a$  was evaluated by fitting the rate constants determined by Eq. (1) to the Arrhenius equation, using the following data

t, °C	400	425	450	475	500
<i>K</i> , nm <sup>2</sup>	7.52	12.69	23.48	39.77	72.09

In this way,  $E_a$  was found to be 97 kJ/mol.



Fig. 1. Isotherms of  $V_2S_5$ /InP oxidation in oxygen (Kröger-Ziegler plots) at (1) 400, (2) 425, (3) 450, (4) 475, and (5) 500°C.



Fig. 2. P  $L_{2,3}$  x-ray emission spectra for the products of  $V_2S_5/InP$  oxidation (a) at 425°C for 60 min, (b) at 475°C for 15 min, and (c) at 475°C for 30 min.

To gain a more detailed insight into the processes involved in the thermal oxidation of  $V_2S_5/InP$  structures, these were characterized by x-ray energy spectroscopy (XES) and IR spectroscopy. XES provides information about the energy spectrum of valence electrons and, hence, about the character of interatomic interactions in the layer during oxidation. With this technique, the electronic states of different symmetry in the valence and conduction bands can be studied separately (emission and absorption spectra, respectively).

X-ray spectra were taken with an RSM-500 spectrometer. The residual pressure in the x-ray tube was  $(2-5) \times 10^{-4}$  Pa. The pressure in the spectrometer chamber was one order of magnitude higher. The probe depth was ≤50-80 nm. XES data were used to assess the distribution of P 3s states over the valence band. Figure 2 displays the P  $L_{2,3}$ -ray emission spectra of the structures oxidized under different conditions. Unfortunately, the resolution in these spectra is not high enough to identify any particular compounds. In view of this, attempts were made to decompose the spectra using reference spectra of InP, P,  $InPO_4$ , and  $InPS_4$ . It is of interest to note the broadening of the band around 120 eV and the absence of the emission at 126 eV characteristic of the P-P bond (Fig. 2, spectra 2b, 2c) [4], indicating the formation of P-V low-polarity bonds. The presence of these bonds in the oxygen-deficient material (the absence of the prominent signal at 126-127 eV) suggests the formation of a vanadium sulfide phosphide  $VP_xS_y$ , in which the V atoms are coordinated to both S and P. This type of compound was also taken into account in decomposing the spectra.

The results of XES characterization are summarized in the table.

A noteworthy feature of these data is that the InPS<sub>4</sub> and P contents of the layer decrease markedly with increasing oxidation temperature. The decrease in InPS<sub>4</sub> content correlates well with the reported thermodynamic instability of InP + InPS<sub>4</sub> mixtures, resulting in the formation of indium phosphorus sulfides [5]. The decrease in phosphorus content is attributable to the reaction of P with V<sub>2</sub>S<sub>5</sub>, yielding VP<sub>x</sub>S<sub>y</sub>. An important point is that the phosphorus in VP<sub>x</sub>S<sub>y</sub> is coordinated to vanadium rather than to sulfur.

Additional information on the composition of the grown layers was obtained by IR spectroscopy (SPECORD-IR-75 spectrophotometer, 400–1400 cm<sup>-1</sup>). The spectra were corrected for absorption by air. Figure 3 displays the IR absorption spectra of the films prepared by thermal oxidation under different conditions. The IR absorption data strongly suggest that, in the initial stage of the process,  $V_2S_5$  oxidizes according to the scheme  $V_2S_5 \longrightarrow (VO_2)_2SO_4 \longrightarrow V_2O_5$ . Indeed, the observed prominent features at 896 and 925 cm<sup>-1</sup> [6] are characteristic of the  $VO_2^+$  group [6], and the absorptions at 1118 and 1058 cm<sup>-1</sup> arise from the  $SO_4^{2-}$  bidentate group. The spectra of the films oxidized at 475°C (Figs. 3b, 3c) contain a weak feature at 805 cm<sup>-1</sup>, indicating the formation of  $V_2O_5$ . With increasing oxi-

INORGANIC MATERIALS Vol. 36 No. 10 2000

dation temperature or time, the In content of the films increases. The absorptions at 565 and 535 cm<sup>-1</sup> testify to the presence of indium oxide [8]; the intensity of these features rises with oxidation temperature. Since increasing the oxidation temperature or time promotes the transformation of  $(VO_2)_2SO_4$  into  $V_2O_5$ , accompanied by a decrease in the concentration of sulfate groups, we suppose that the broadening of the signal is due to the gradual enrichment of the growing layer in In<sub>2</sub>O<sub>3</sub>.

Thus, the IR absorption data demonstrate that the primary product of  $V_2S_5$  oxidation is vanadyl sulfate,  $(VO_2)_2SO_4$ , which transforms into  $V_2O_5$  with increasing oxidation temperature or duration. Therefore, the oxidation of  $V_2S_5$ /InP structures proceeds according to the scheme  $V_2S_5 \longrightarrow (VO_2)_2SO_4 \longrightarrow V_2O_5$ . With increasing oxidation temperature or duration, the In<sub>2</sub>O<sub>3</sub> content of the film increases (Fig. 3). It seems likely that the formation of  $In_2O_3$  is the major cause for the observed weight gain of the film, since, according to the IR data, the only absorptions growing with oxidation temperature and time are those due to  $In_2O_3$ . We suppose that  $In_2O_3$  is formed by the following mechanism: In addition to the reaction of indium with oxygen, the products of V<sub>2</sub>S<sub>5</sub> oxidation are likely to transport oxygen to the substrate:

$$4 \ln + 3 V_2 O_5 = 2 \ln_2 O_3 + 3 V_2 O_3, \qquad (2)$$

$$2In + (VO_2)_2 SO_4 = In_2O_3 + V_2O_3 + SO_2.$$
(3)

The processes occurring at the film–substrate interface can be inferred from XES data, which demonstrate that  $V_2S_5$  reacts actively with InP, as represented by the following reaction schemes:

$$InP = In + P, \qquad (4)$$

$$V_2S_5 = V_2S_3 + 2S,$$
 (5)

$$V_2S_5 + 2In = 2VS + In_2S_3,$$
 (6)

$$InP + 4S = InPS_4, \tag{7}$$

$$3 \ln PS_4 + 5 \ln P = 4 \ln_2 S_3 + 8 P,$$
 (8)

$$VS + (x - 1)S + yP = VP_xS_y, \qquad (9)$$

$$2InP + V_2S_5 = In_2S_3 + 2VPS.$$
(10)

The major stable products of reactions (4)–(10) are probably  $In_2S_3$  and  $VP_xS_y$ .

As is evident from the table, the notable decrease in the  $InPS_4$  and P contents of the layer with increasing

INORGANIC MATERIALS Vol. 36 No. 10 2000



Fig. 3. IR absorption spectra of the films obtained by thermal oxidation of  $V_2S_5/InP$  structures (a) at 425°C for 60 min, (b) at 475°C for 15 min, and (c) at 475°C for 30 min.

temperature correlates well with the thermodynamic instability of  $InP + InPS_4$  mixtures, converting into indium phosphorus sulfide. The decrease in the content of elemental phosphorus is attributable to the reaction with  $V_2S_5$ , yielding  $VP_xS_y$ . As mentioned above, the phosphorus in VP<sub>r</sub>S<sub>y</sub> is coordinated to vanadium rather than to sulfur. It also follows from the data in the table that, independent of temperature, increasing the oxidation duration increases the contents of oxygen and InPO<sub>4</sub>. Note that InPO<sub>4</sub> was not revealed by IR spectroscopy, presumably because its content in the oxide layer was too low. Given that the oxygen affinity of phosphorus is by far more pronounced than those of sulfur, indium, and vanadium, we suppose that the free phosphorus is located mainly in the oxygen-deficient region—near the film-substrate interface.

Composition of the layers prepared by thermal oxidation of  $V_2S_5$ /InP structures (XES data)

Oxidation	Weight percent						
conditions	InP	InPS <sub>4</sub>	P <sub>cr</sub>	VS <sub>x</sub> P <sub>y</sub>	InPO <sub>4</sub>		
425°C, 60 min	10.4	9.6	14.1	16.3	29.6		
475°C, 15 min	32.9	17.1	8.6	34.3	7.1		
475°C, 30 min	27.1	14.3	8.3	37.6	12.8		

## CONCLUSION

Our XES and IR spectroscopy data demonstrate that the oxidation of  $V_2S_5/InP$  structures proceeds rapidly into the film bulk and initially follows the reaction scheme  $V_2S_5 \longrightarrow (VO_2)_2SO_4 \longrightarrow V_2O_5$ . As a result, a dense oxide-sulfate layer is formed on the substrate surface, preventing oxygen diffusion to the film-substrate interface. As in the PbS/InP and Sb<sub>2</sub>S<sub>3</sub>/InP systems, the sulfide activator transfers sulfur to In to form  $In_2S_3$ . The formation of a dense  $In_2S_3$  layer near the interface hinders phosphorus diffusion to the surface, thereby inhibiting its oxidation. A characteristic feature of the process is the formation of vanadium sulfide phosphide. With increasing oxidation temperature and/or duration, the In content of the film increases, and In reacts with vanadyl sulfate to form In<sub>2</sub>O<sub>3</sub>. This reaction stage, limited by In diffusion, is responsible for most of the increase in film thickness.

### REFERENCES

- 1. Inorganic and Theoretical Chemistry, Mellor, J.W., Ed., London: Longmans, 1947, vol. 8, pp. 911–915.
- 2. Karyakin, Yu.V. and Angelov, I.M., Chistye khimicheskie veshchestva. Rukovodstvo po prigotovleniyu neorganicheskikh reagentov i preparatov v laboratornykh uslo-

viyakh (Pure Chemical Substances: A Guide to the Preparation of Inorganic Reagents and Systems under Laboratory Conditions), Moscow: Khimiya, 1974.

- 3. Tret'yakov, Yu.D., *Tverdofaznye reaktsii* (Solid-State Reactions), Moscow: Khimiya, 1974.
- Andreev, V.M., Alakhverdiev, A.M., Ivent'eva, O.O., et al., Photoluminescent Properties and Electronic Structure of the Anodized InP Surface, *Fiz. Tonkikh Ple*nok, 1985, vol. 19, no. 1, pp. 110–115.
- Mittova, I.Ya., Pukhova, V.V., Klement'eva, I.F., et al., Preparation of GaAs/Bi<sub>2</sub>S<sub>3</sub> Structures by Thermal Oxidation and Properties of Dielectric Films on GaAs, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1988, vol. 24, no. 9, pp. 1431–1434.
- Yurchenko, E.N., Kustova, G.N., and Batsanov, S.S., Kolebatel'nye spektry neorganicheskikh soedinenii (Vibrational Spectra of Inorganic Compounds), Novosibirsk: Nauka, 1981.
- Nakamoto, K., Infrared and Raman Spectra of Inorganic and Coordination Compounds, New York: Wiley, 1986. Translated under the title IK-Spektry i spektry KR neorganicheskikh i koordinatsionnykh soedinenii, Moscow: Mir, 1991.
- Yamaguchi, M., Replay to "Comments on Thermal Oxidation of InP and Properties of Oxide Films," J. Appl. Phys., 1982, vol. 53, no. 3, pp. 1834–1835.