Inorganic Materials, Vol. 38, No. 6, 2002, pp. 576–581. Translated from Neorganicheskie Materialy, Vol. 38, No. 6, 2002, pp. 700–705.
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Metalorganic Chemical Vapor Deposition of Antimony Oxide Films on Semiconductor Substrates

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Received October 29, 2001

Abstract—The growth kinetics of oxide films on silicon and gallium arsenide substrates were studied, using alkyl and alkoxide metalorganic precursors (triethylantimony, tripropylantimony, antimony butoxide, and antimony tri-β-aminoethoxide). The effect of thermal annealing on the microstructure and properties of the films was examined. Analysis of the deposition kinetics, composition, and properties of the films demonstrates that metalorganic chemical vapor deposition in an oxidizing atmosphere, using antimony butoxide or triethylantimony as a precursor, enables the growth of insulating layers on Si and GaAs at low temperatures (130–300°C).

INTRODUCTION

Metalorganic chemical vapor deposition (MOCVD) plays an important role in the fabrication of semiconductor devices and integrated circuits on III–V substrates because these may decompose at relatively low temperatures. The low structural perfection of thermal oxide layers on gallium arsenide stimulates a search for low-temperature methods of growing oxide films on this material. During the growth of thermal oxide on GaAs, only a small amount of arsenic is incorporated into the film; the major portion of the arsenic accumulates at the film–substrate interface [1]. If the vapor phase contains MO compounds of Group V elements (e.g., Sb and Bi), these may substitute for arsenic in the GaAs substrate, and subsequent oxidation of such structures will notably improve the quality of the oxide film.

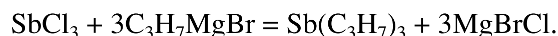
In earlier studies, to produce aluminum, gallium, and indium oxide films by MOCVD, use was made of metal alkyl and alkoxide precursors [2]. There are, however, no reports dealing with the deposition of antimony oxide films. Powell *et al.* [3] and Anokhin *et al.* [4] deposited alumina and indium oxide films via pyrolysis of trialkyl compounds. For other metal oxides, alkyl compounds were not used because they are extremely reactive with air and moisture. A safer procedure for depositing gallium oxide films was proposed by Vishnyakov *et al.* [5], who used a solution of trimethylgallium in diethyl ether. Since alkyls contain no oxygen, the process must be run in an oxidizing atmosphere. This is not necessary with metal alkoxides, which are often used as precursors for MOCVD of oxide films. In particular, alumina films were deposited in a number of studies [5–9] using aluminum isopropoxide. Note that it is of considerable interest to extend the range of alkoxides suitable for producing oxide layers, since these precursors are safe to handle and allow one to deposit oxide films without introducing oxygen into the reactor.

The objective of this work was to grow antimony oxide films on semiconductor substrates by MOCVD using alkyl (triethylantimony and tripropylantimony) and alkoxide (antimony butoxide and antimony tri-β-aminoethoxide) precursors and to examine the effect of subsequent annealing on the composition, structure, and properties of the films.

EXPERIMENTAL

The boiling points and refractive indices of the MO precursors synthesized by the procedures described below differed very little from those reported earlier [10]. All of the starting chemicals used were of reagent grade.

Tripropylantimony was synthesized by reacting $SbCl_3$ with propylmagnesium bromide in flowing inert gas:



$$SbCl_3 + 3C_3H_7MgBr = Sb(C_3H_7)_3 + 3MgBrCl.$$

First, propylmagnesium bromide was prepared by reacting magnesium with propyl bromide. To this end, magnesium filings (12 g) were placed in a solution of propyl bromide (45 ml) in diethyl ether (150 ml). The resultant propylmagnesium bromide was then introduced into a three-neck flask fitted with a stirrer, reflux condenser with a $CaCl_2$-filled jacket, dropping funnel, and inlet for inert gas. After the flask was cooled to 0°C, a solution of $SbCl_3$ (38 g) in diethyl ether (150 ml) was added with stirring. The mixture was boiled for 30 min and then, after cooling to 0°C, transferred to a separatory funnel. After removing the uppermost layer, it was vacuum-distilled to give tripropylantimony.

† Deceased.

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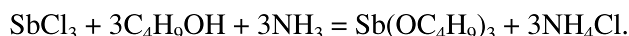
Triethylantimony was synthesized in a similar way, by reacting $SbCl_3$ with ethylmagnesium bromide in flowing inert gas.

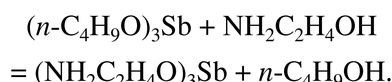
Antimony butoxide was prepared by reacting $SbCl_3$ with butyl alcohol in the presence of ammonia:



$$SbCl_3 + 3C_4H_9OH + 3NH_3 = Sb(OC_4H_9)_3 + 3NH_4Cl.$$

To this end, $SbCl_3$ (228 g) and absolute butyl alcohol (550 ml) were mixed in a three-neck flask fitted with a stirrer, condenser, and an inlet tube for ammonia. After cooling to 0°C, ammonia was bubbled through the mixture. The precipitating ammonium chloride was then collected on a filter. The filtrate was vacuum-distilled to separate antimony butoxide.

Antimony tri-β-aminoethoxide was prepared via transesterification of antimony butoxide with ethyl Cellosolve and ethanolamine:



$$(n\text{-}C_4H_9O)_3Sb + NH_2C_2H_4OH$$
$$= (NH_2C_2H_4O)_3Sb + n\text{-}C_4H_9OH.$$

Antimony butoxide (5 g) and a small excess of ethanolamine were introduced into a vacuum-distillation flask. After distilling off the butyl alcohol, the resultant antimony tri-β-aminoethoxide was vacuum distilled.

The substrates used in kinetic studies were polished wafers of AGP-1 and AGChTs GaAs(100) with a carrier concentration of 10^{16} cm^{-3} and KEF Si with an electrical resistivity of 7.5 Ω cm. The process was run in a resistance-heated two-zone furnace. The temperature was maintained with a stability of ±1°C. The source and deposition temperatures were chosen using thermogravimetric data (Paulik–Paulik–Erdey system).

We used single- and two-zone procedures. In the former case, the MO precursor (antimony butoxide, tripropylantimony, or antimony tri-β-aminoethoxide) was placed in a quartz container, which was then covered with the substrate. In the two-zone procedure, the container with the precursor (triethylantimony) was situated in the lower temperature zone, where the precursor vaporized without decomposition, and the substrate was located in the higher temperature zone, where the precursor decomposed.

Given that antimony alkyl compounds are unstable in air and extremely reactive, we used their solutions in butyl alcohol or toluene. In the case of triethylantimony, we employed solutions with $Sb(C_2H_5)_3 : C_4H_9OH = 1 : 1$ or $2 : 1$ and $Sb(C_2H_5)_3 : C_6H_5CH_3 = 1 : 1$ by volume. The solution temperature was 90°C, and the substrate (Si or GaAs) temperature was 130, 190, or 300°C. This range of deposition temperatures was chosen because, below 130°C, no film growth occurred, while, above 300°C, the deposition rate was too high, resulting in poor bonding between the film and the substrate. The flow rate of argon carrier gas was 18 l/h in all deposition runs.

The etching behavior of the films was studied using 7.2% hydrochloric acid. To study the effect of thermal annealing on the film microstructure and properties, the films deposited in an argon atmosphere were then annealed for 30 min at 300, 350, and 400°C in oxygen, a mixture of oxygen and water vapor, or argon.

Film thicknesses were measured with an E-3 ellipsometer to an accuracy of ±1 nm. Film composition was determined by IR spectroscopy (UR-20 instrument), electron diffraction (EG-100A unit), and electron probe x-ray microanalysis (Camscan SI scanning electron microscope equipped with a Link AN10/55 energy-dispersive x-ray analysis system). The surface morphology of the films was examined using an MII-4 interference microscope and ARM-1000 electron microscope.

RESULTS AND DISCUSSION

Our results on the kinetics of film deposition via thermal decomposition of triethylantimony are summarized in Table 1 and Fig. 1. The film thickness was found to vary linearly with deposition time. Preliminary experiments showed that the deposition rate depended strongly on whether the solution was used as-prepared or after storage. The nature of the substrate had no significant effect on the deposition rate, which is, in addition, almost temperature-independent (Table 1). This may be due to the fact that the MO precursor fully decomposes even at 130°C, and the deposition rate is then controlled by the flow rate of the carrier gas [1]. In the case of the pyrolysis of a triethylantimony solution in toluene, the growth rate even decreases with increasing temperature. Increasing the triethylantimony concentration in butyl alcohol slightly increases the deposition rate (Fig. 1). The rate constants for the pyrolysis of solutions with $Sb(C_2H_5)_3 : C_4H_9OH = 1 : 1$ and $2 : 1$ differ insignificantly: 6 ± 0.4 and 7 ± 0.8 nm/min.

Interestingly enough, the refractive index of the films is essentially independent of the nature of the solvent and substrate and increases with deposition temperature, pointing to changes in film composition (Table 1). The refractive index varies from 1.67 to 2.06,

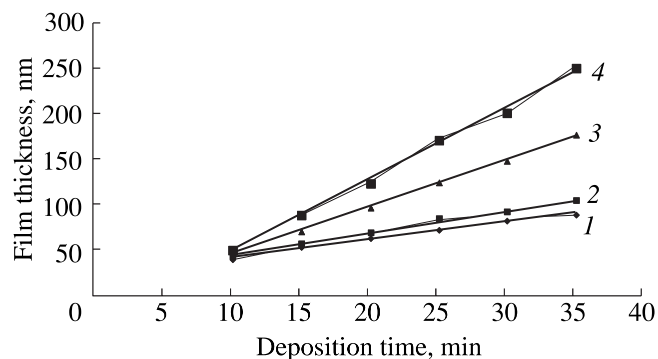


Fig. 1. Film thickness as a function of deposition time for films deposited on GaAs via triethylantimony pyrolysis at (*1*, *3*, *4*) 190 and (*2*) 130°C and an $Sb(C_2H_5)_3 : C_4H_9OH$ ratio of (*1*–*3*) 1 : 1 and (*4*) 2 : 1; (*1*, *2*) 30 min after solution preparation, (*3*, *4*) freshly prepared solution.

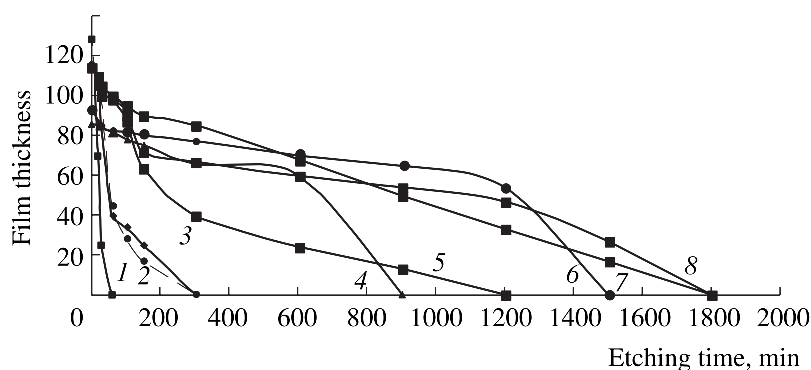


Fig. 2. Film thickness as a function of etching time in 7.2% hydrochloric acid for films deposited on (*1–6*, *8*) GaAs and (*7*) Si at (*1*, *3*) 130, (*2*, *5*, *7*, *8*) 190, and (*4*, *6*) 300°C via triethylantimony pyrolysis at (*1*, *2*) $Sb(C_2H_5)_3 : C_6H_5CH_3 = 1 : 1$, (*3–7*) $Sb(C_2H_5)_3 : C_4H_9OH = 1 : 1$, and (*8*) $Sb(C_2H_5)_3 : C_4H_9OH = 2 : 1$; (*4*) oxygen annealing at 300°C for 20 min.

which corresponds to different Sb_2O_4 polymorphs [11]. According to x-ray microanalysis data, the films on GaAs consist of Sb and O, and those on Si contain, in addition, carbon. The IR spectra of the films show an absorption band at 820 cm^{-1}, due to the Sb–O bond [12].

The backside and frontside of the films were found to differ in etching rate (Fig. 2). Moreover, the etching rate of the films produced using triethylantimony solutions in toluene is much faster than that of the films deposited from solutions in butyl alcohol. The etching rate also depends on the initial triethylantimony concentration: at higher concentration, the etching rate is slower. The etching behaviors of the films deposited on Si and GaAs are similar. The only difference is that the backside of the films grown on GaAs dissolves more rapidly, which is attributable to the diffusion of Ga and As into the film. With increasing deposition temperature, the etching rate of the frontside decreases; the same is observed after annealing. MOCVD films typically contain residual organics and trace amounts of

Table 1. Properties of the films deposited on GaAs and Si using triethylantimony

Solution	*t*, °C	Substrate	τ, min	*d*, nm	*n*	*v*, nm/min
$Sb(C_2H_5)_3 : C_4H_9OH = 1 : 1$ (after 30-min storage)	130	AGP GaAs	15–40	64–113	1.67–1.73	3–4
	190	AGP GaAs	15–50	54–113	1.75–1.95	2–4
	300	AGP GaAs	30	84	2.03	3
$Sb(C_2H_5)_3 : C_4H_9OH = 1 : 1$ (as-prepared)	190	AGP GaAs	11–25	40–122	1.68–1.86	4–5
$Sb(C_2H_5)_3 : C_4H_9OH = 2 : 1$ (as-prepared)	190	AGP GaAs	8–30	39–191	1.76–2.68	5–6
	190	KEF Si	10–20	53–92	1.76–1.78	5
$Sb(C_2H_5)_3 : C_6H_5CH_3 = 1 : 1$ (as-prepared)	130	AGP GaAs	15–30	109–294	1.65–2.18	6–10
	190	AGP GaAs	15	116	1.69	8
	190	KEF Si	15	102	1.72	7
	300	AGChTs GaAs	30	108	2.03	4
	300	KEF Si	30	94	1.98	3

Table 2. Effect of annealing in argon atmosphere on the thickness and refractive index of films deposited on GaAs using a 1 : 1 solution of $Sb(C_2H_5)_3$ in C_4H_9OH

t_{pyr}, °C	t_{ann}, °C	Gas phase	τ_{ann}, min	d, nm	n	d, nm	n
				before annealing		after annealing	
130	400	O_2	20	78	1.69	36	1.88
130	400	O_2	30	95	1.67	34	1.84
130	400	$H_2O(g) + O_2$	20	95	1.67	46	1.85
190	400	O_2	20	108	1.81	81	1.90
190	400	O_2	30	108	1.81	74	1.83
190	400	$H_2O(g) + O_2$	20	108	1,81	75	1.86
190	400	$H_2O(g) + O_2$	20	108	1.81	85	1.78
300	350	O_2	20	90	2.0	94	2.05
300	350	O_2	20	84	2.03	82	2.03
300	350	$H_2O(g) + O_2$	20	90	2.0	87	2.0
300	350	Ar	20	90	2.0	88	2.01
300	400	Ar	20	84	2.03	73	2.02

water [1], which are removed in the course of thermal annealing, which, accordingly, raises the film density and improves the film–substrate adhesion.

Table 2 lists the thicknesses and refractive indices of the films before and after annealing in different atmospheres. Both in oxygen and water vapor, annealing reduces the thickness and increases the refractive index of the films deposited at 130 and 190°C, while those of the films grown at 300°C remain virtually unchanged.

Annealing was found to have different effects on the microstructure of the films deposited at high and low temperatures. The films deposited at 300°C and annealed at 400°C were nonuniform in thickness: in some regions, the film thickness was larger than that before annealing. This effect seems to be due to further oxidation of the partially oxidized antimony during annealing. At annealing temperatures below 400°C, this effect was not detected. The films grown at 130 and 190°C were uniform in thickness after annealing at any temperature. The compositions of the films before and after annealing, as determined by x-ray microanalysis, are listed in Table 3.

The electric strength of the films grown on GaAs and Si using triethylantimony rises with deposition temperature and is higher when toluene is used as the solvent (Table 4). The nature of the substrate has an insignificant effect on the electrical properties of the films.

We failed to produce antimony oxide films by MOCVD in oxygen or air using tripropylantimony. Only in a mixture of H_2O and O_2 were deposition runs successful. The thickness of the film deposited in 2 min was 200 nm. Deposition kinetics of such films were not studied because tripropylantimony is difficult to synthesize.

Table 3. Effect of annealing on the composition of films deposited via triethylantimony pyrolysis (x-ray microanalysis on a Camscan SI scanning electron microscope equipped with a Link AN10/55 energy-dispersive x-ray analysis system)

Substrate	Deposition/annealing temperature	Analyte	Atomic percent		
			Sb	O	C
GaAs	190°C	Film	62	38	–
	190°C, annealing at 400°C	Film	60	40	–
	Same as above	Island	57	43	–
	300°C	Film	56	44	–
	300°C, annealing at 400°C	Island	54	46	–
Si	190°C, annealing at 400°C	Island	45	43	12

Table 4. Electric strength and refractive indices of films deposited via triethylantimony pyrolysis

MO precursor	Substrate	t, °C	d, nm	n	$E_{br} \times 10^{-5}$, V/cm
$Sb(C_2H_5)_3 : C_4H_9OH = 1 : 1$	AGChTs GaAs(100)	190	90	1.72	3
	AGChTs GaAs(100)	190	108	1.84	1.4
	KEF Si(111)	190	75	1.75	37
	AGChTs GaAs(100)	300	95	2.01	5.3
$Sb(C_2H_5)_3 : C_6H_5CH_3 = 1 : 1$	AGChTs GaAs(100)	300	108	2.03	9.3
	KEF Si(111)	300	94	1.98	8.5

Alkoxide precursors offer a number of advantages over alkyls: they are cheaper, much more stable in air, and safer in handling. In our preparations, insulating layers were for the first time grown on GaAs by MOCVD using antimony butoxide and antimony tri-β-aminoethoxide.

The log–log plots of film thickness vs. deposition time for the antimony butoxide precursor yield straight lines (Fig. 3a), indicating power-law behavior, $d = K^n\tau^n$ [13]. The exponent n is 3.00, 2.94, and 1.75 for the processes at 150, 170, and 190°C, respectively. The apparent activation energy of the deposition process, determined from the Arrhenius plot for K_{av} (Fig. 3b) [13], is 22 kJ/mol. According to x-ray diffraction data, the films deposited with the use of antimony butoxide consist of Sb_2O_3 and are polycrystalline. The films adhere tenaciously to the substrate and have a dielectric strength in the range 8×10^5 to 3×10^6 V/cm.

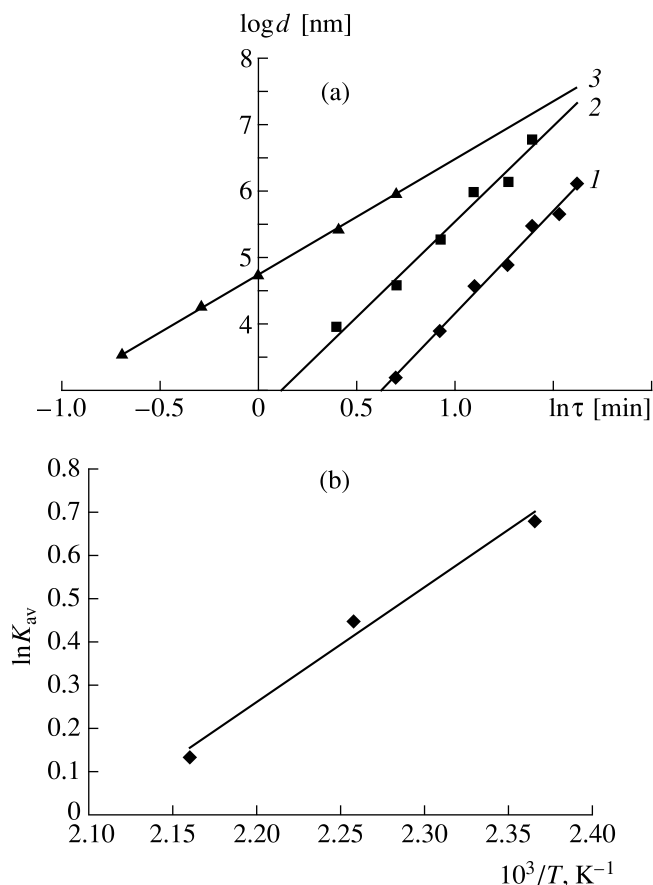


Fig. 3. (a) Log–log plots of film thickness vs. deposition time at (*1*) 150, (*2*) 170, and (*3*) 190°C. (b) Arrhenius plot of K_{av} for film growth on GaAs via antimony butoxide pyrolysis.

Thermal decomposition of tri-β-aminoethoxide in oxygen yielded oxide films even at 200°C, with a deposition rate of 200 nm/min. The grown films loosely adhered to the substrate and were unstable during air storage.

CONCLUSION

Our results demonstrate that MOCVD with the use of triethylantimony in an oxidizing atmosphere is an attractive process for producing insulating layers on silicon and gallium arsenide at low temperatures (130–300°C). The main drawback to this precursor—its instability even at room temperature—can be obviated by using its solutions in toluene or butyl alcohol. The resulting layers consist mainly of pyrolytic antimony oxide and contain a minor amount of carbon.

The use of antimony butoxide as an MO precursor makes it possible to deposit Sb_2O_3 films at low temperatures. As distinct from triethylantimony, this precursor does not require the presence of oxidants in the gas phase and, owing to its stability, facilitates the deposition process.

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