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Mass spectrometric study of laser induced pyrolytic decomposition of TIBA and TMAA

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Abstract: The composition of the gaseous phases during pyrolytic laser-induced chemical vapor deposition (LCVD) of aluminium from triisobutylaluminium (TIBA) and trimethylamine alane (TMAA) (aluminium trihydride trimethylamine) was determined. The analysis was carried out by means of quadrupole mass spectrometer (QMS) in closed reaction cell. The developed arrangement for sampling allowed *in situ* analyses during the LCVD process. The decomposition of the aluminium precursors was induced by copper bromide vapor laser on the surface of (111) silicon monocrystalline wafer at different process parameters (partial pressure, laser power and scanning speed). The analyses showed usual gaseous products for the pyrolysis of TIBA and TMAA and additional species. The occurred pyrolysis products were probably due to different ways of decomposition of the precursors caused by pulsed laser irradiation. The results from this study combined with surface analysis of the deposit could help for better understanding of LCVD and for obtaining of high purity aluminium layers.

1. Introduction

TIBA and TMAA are important precursors for metalorganic chemical vapor deposition (MOCVD) of aluminium [1,2] and compound semiconductors [3,4] and for LCVD of aluminium [5,6]. The properties of the deposited material strongly depend on the decomposition mechanism of precursors which determines the gaseous phase composition and the carbon incorporation into the growing layer [2,3,7]. LCVD of aluminium is based on photolysis or pyrolysis according to the wavelengths of the laser beam. An intensive research concerning UV laser photolysis of aluminium alkyls with product detection has been done by Stuke et al [8]. Tokumitsu et al. present mass spectra for pyrolysis (at 500 °C) and photolysis (using ArF laser) of TIBA and established different decomposition reactions for the two cases [3]. Mass spectrometric studies were used by Bent et al. for investigation of surface chemistry of

aluminium pyrolytic deposition from TIBA [7]. The authors found different thermal decomposition pathways for surfaces heated below and above 600 K with primary products isobutylene and hydrogen, and propylene and hydrogen, respectively. When TMAA is used as aluminium precursor decomposition mechanism leads to formation of trimethylamine and hydrogen [9]. The information in literature concerns moderate temperatures of decomposition. Different mechanisms and products of chemical reaction are expected when laser pyrolysis of TIBA or TMAA takes place on the substrate. Such effect would be more strongly expressed when pulsed laser irradiation with extremely high power density per pulse is used causing high peak surface temperature [10]. This has directed our research to activation of LCVD of aluminium from TIBA and TMAA by such a laser for high temperature pyrolysis [11,12]. The mass spectrometric study of pyrolytic decomposition of these aluminium precursors with pulsed visible laser could help for better understanding of the processes.

2. Experimental

The experimental set-up for LCVD of aluminium has been described in earlier papers [11]. A quadrupole mass spectrometer QUADREX-200 (LEYBOLD-INFICON) equipped with a Faraday cup was attached to the rig. The mass spectrometer can scan over a range from 1 amu to 200 amu. The rated sensitivity of unit is 6.5×10^{-11} mbar for N_2 and ionization energy is 70 eV. The experimental arrangement for sampling the gaseous products during laser pyrolysis is shown on Figure 1. A sampling capillary is introduced into the stainless steel cell approaching the surface of (111) silicon monocrystalline wafer on which the pyrolysis takes place. A high vacuum gas dosing needle valve (BALZERS) was attached to the end of this capillary for precise and reproducible control of pressure in QMS sensing head.

TIBA (SHERING product) purified by vacuum distillation and TMAA synthesized according to the published procedures [13] were used as source materials. Their pyrolysis was caused by focused up to 130 μm beam of a copper bromide vapor laser with wavelengths of 510 and 578 nm, repetition frequency 20 kHz and pulse length 60 ns. The experiment itself includes the following steps: putting the cleaned silicon wafer into the cell; evacuation up to 10^{-4} Pa; introduction of TIBA or TMAA with desired partial pressure and starting computer program for scanning the substrate. The incident laser power of 2.75 W and 1.3 W was enough to cause high rate pyrolysis of TIBA and TMAA, respectively, producing aluminium stripe deposited on the substrate surface and gaseous products detected by QMS.

Figure 1 Experimental set-up for LCVD coupled with quadrupole mass spectrometer for *in situ* analysis

3. Results and discussion

3.1. TIBA

The obtained room temperature mass spectrum of TIBA showed pattern similar to those presented by Tokumitsu et al. [3]. The detected characteristic peaks at $m/e = 56, 55, 43, 41, 40, 39, 29, 28, 27$ are assigned to the fragments $C_4H_8^+/AlC_2H_5^+$, $C_4H_7^+/AlC_2H_4^+$, $C_3H_7^+/AlHCH_3^+$, $C_3H_5^+/AlCH_2^+$, $C_3H_4^+$, $C_3H_3^+$, $C_2H_5^+/AlH_2^+$, $C_2H_4^+/AlH^+$, $C_2H_3^+/Al^+$, respectively.

Figure 2 shows a mass spectrum of the gaseous products released during laser pyrolysis of TIBA, obtained after 250 s time of laser processing. The 'bar-subtract' mass spectrum illustrates the differences between the current data and the previously saved data which were obtained right before the beginning of the pyrolysis. As presented on Figure 2 the basic mass peaks changing their intensities are $m/e = 41, 39, 56, 28, 27, 55, 29, 40, 2$. These peaks are typical for the mass spectra of isobutylene and hydrogen [14]. Their presence when pyrolysis of TIBA takes place has been described in literature [3,7]. In accordance with the table data of isobutylene the intensity of mass peak at $m/e = 39$ should be 1.02 times higher than that at $m/e = 56$ [14]. The estimation of this ratio from Figure 2 shows value of 1.20. This discrepancy is probably due to simultaneous presence of fragments with $m/e = 39$ originated from the molecules of isobutylene and propylene [14]. According to the model presented by Bent et al. there are two possible reaction mechanisms for decomposition of TIBA: β -hydride elimination (at temperatures below 600 K) and β -methyl elimination (at temperatures above 600 K) [7]. We are not clear about what parameters of LCVD process favour the formation of each of the gaseous products isobutylene and propylene. However it should be stressed that the laser pyrolysis occurs at higher temperature gradients on the substrate surface compared with the moderate temperature pyrolysis of aluminium alkyls described in literature. The Gaussian

Figure 2 Bar-subtract mass spectrum of products from TIBA pyrolysis after 250 s laser processing time at 207 MW/m² average power density, 40 μ m/s scanning speed and 600 Pa (6 mbar) TIBA

distribution of temperature within the laser spot and surface temperature oscillations probably cause different pyrolysis mechanism of TIBA in the center and at the edge of microreaction zone. This could result in simultaneous decomposition of TIBA by both mentioned mechanisms with formation of different gaseous products. β -methyl elimination has a substantial contribution to carbon incorporation in the growing layers detected by Auger electron spectroscopy.

3.2. TMAA

The detected characteristic peaks for room temperature mass spectrum of TMAA at $m/e = 59, 58, 56, 42, 30, 28, 27, 15$ could be assigned to the fragments $N(CH_3)_3^+$, $N(CH_3)_2CH_2^+$, $N(CH_2)_3^+$, $N(CH_2)_2^+$, NCH_3H^+/AlH_3^+ , NCH_2^+/AlH^+ , NCH^+/Al^+ , CH_3^+ , respectively.

Figure 3 shows 'bar-subtract' mass spectrum of the gaseous products released during laser pyrolysis of TMAA, obtained after 1000 s time of laser processing. As presented on Figure 3 the basic mass peaks changing their intensities are $m/e = 58, 42, 59, 15, 30, 28, 43, 41, 2$. These peaks indicate formation of usual products of TMAA decomposition - trimethylamine and hydrogen [14]. In accordance with the table data of trimethylamine the intensity of mass peak at $m/e = 58$ should be 2.9 times higher than that at $m/e = 15$ [14]. The estimation of this

Figure 3 Bar-subtract mass spectrum of products from TMAA pyrolysis after 1000 s laser processing time at 98 MW/m² average power density, 10 μ m/s scanning speed and 10 Pa (0.1 mbar) TMAA

ratio from Figure 3 shows value of 1.3. This discrepancy is probably due to simultaneous presence of fragments with $m/e = 15$ originated from the molecules of trimethylamine and methane [14]. The mass peak at $m/e = 16$ indicates presence of methane in gaseous phase during LCVD of Al from TMAA. In our experiments we admit a release of CH_3 groups in the gaseous phase which could interact with hydrogen to form CH_4 detected by QMS. This assumption is based on the unusual fragmentation which could be caused by laser with pulsed time structure. In the case of copper bromide vapor laser used in this work the power density for the time of a single pulse is about 183 GW/m². As a result the surface temperature in microreaction zone on the substrate could achieve values substantially exceeding those considered for pyrolysis of aluminium alkyls in literature. Tremendous energy flux is absorbed by the substrate and probably changes the decomposition mechanism compared with that at moderate temperatures. At high surface temperature the liberation of CH_3 groups is possible due to the break of nitrogen-carbon bond. A secondary gas phase reaction of CH_3 groups is quite likely to form CH_4 which is shown on Figure 3 ($m/e = 16$). It is necessary to consider the element analysis of the deposit in order to create a complete model of laser pyrolysis mechanism of TMAA. Such experiments using X-ray photoemission spectroscopy and Auger electron spectroscopy are in progress.

4. Conclusions

Pyrolytic decompositions of TIBA and TMAA on silicon substrate using copper bromide vapor laser were studied. The gaseous products determined *in situ* by QMS during LCVD of Al from TIBA are isobutylene, propylene and hydrogen, and trimethylamine, methane and hydrogen in the case of TMAA. Simultaneous presence of isobutylene and propylene when TIBA is used and formation of methane as a result of TMAA decomposition are unusual for the conventional pyrolysis of these precursors at moderate temperature. We believe this is due to the pulsed visible laser which supplies tremendous power density to the surface in dwell time.

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