Thin Solid Films 575 (2015) 47–51

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# Formation of alumina film using alloy catalyzers in catalytic chemical vapor deposition

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ARTICLE INFO

Available online 13 October 2014

*Keywords:*
Alumina film
Alloy catalyzer
Decomposition of TMA
Cat-CVD
Hot-wire CVD
$Al_2O_3$
Passivation film
Barrier film

ABSTRACT

The decomposition of tri-methyl aluminum (TMA) by various catalytic alloys is investigated to find low cost and oxidation-resistive catalyzers for preparation of alumina films by catalytic chemical vapor deposition (Cat-CVD) method. It is found that the temperature to decompose TMA in catalytic decomposition process decreases in the temperature region below 500 °C with associated reduction in activation energy as chromium (Cr) contents in catalytic alloys increase. It is also found that the density of decomposed species increases as nickel (Ni) contents in alloys increase. It has been confirmed from alumina film formation experiments using various alloy catalyzers that the growth rate of films increases as Ni contents included in the catalytic alloys increase.



## 1. Introduction

Alumina films have excellent inherent properties such as high dielectric constant [1], large energy gap [2,3], good tolerance for high temperature operation [4], high gas-barrier property for oxygen and steam, hard to be broken, high light transmission rate and non-toxicity. Therefore, alumina films have recently been studied to adapt them for use as surface passivation films in crystalline Si solar cells [5–15] and gas barrier films in organic materials [16]. Industries dealing with these products demand low cost alumina films in addition to low temperature deposition on organic materials. These requirements may be satisfied by Cat-CVD which has such merits as film formation with no plasma induced-damages, low equipment cost and low temperature process [17–25]. However, alumina formation process requires catalyzer materials with resistance to oxidation. Therefore, Saito et al. suggested adopting iridium (Ir) catalyzer to form $SiO_2$ films [26]. Alumina films have been successfully formed by Cat-CVD using tri-methyl aluminum (TMA) and $O_2$ with iridium as the catalyzer material [15,25, 27–29]. However, the cost of $1000/m of Ir wire is too expensive to form low cost alumina films. Ogita et al. have found some alloys such as Chromel and SUS-304 alloys as catalyzers having excellent oxidation resistance [29,30].

In this study, first, the decomposition of TMA using five kinds of alloys such as Alumel, Moleculoy, Inconel X-750, Hastelloy C-276 and SUS-316 has been attempted. Secondly, the formation of alumina films by Cat-CVD using TMA and $O_2$ has been attempted using catalyzers mentioned above. The five alloys mentioned above are selected as candidates of catalyzers as they satisfy four requirements such as resistance to oxidation, low cost below $10/m, inclusion of Ni and/or Cr inside, and melting temperatures above 1000 °C. The requirement for inclusion of Ni and/or Cr is due to the reason why TMA is decomposed by using Chromel and SUS 304 alloys as catalyzers, both containing Ni and/or Cr, known from the previous experiments [29]. The decomposition of TMA using five alloy catalyzers (contents of Cr and/or Ni in respective alloy are given in Figs. 3 and 9) mentioned above was carried out in order to identify three indices to characterize the catalyzers, viz., the decomposition temperature ($T_d$), the activation energy ($E_a$) and the decomposition intensity as well as to determine the origin of decomposition of TMA in the alloy materials. The catalysis process due to inclusion of Cr in the alloys is discussed in relationship with the decomposition temperature, the activation energy and the amount of species decomposed from TMA. The deposition of alumina films on Si by Cat-CVD using such alloys described above was carried out in order to obtain the deposition rate and to find the origin that determines the deposition rate in the catalyzers. The catalysis process due to Ni contained in the alloys is considered in relationship with the deposition rate and the decomposition intensity obtained.

## 2. Experimental

The equipment used in this experiment is shown in Fig. 1. Molecules and atoms decomposed from TMA using alloy catalyzers were identified from the mass measured by the quadrupole mass spectrometer (QMS) attached to the Cat-CVD chamber. The QMS was composed of cross-beam ion source and operated at the electron energy of 100 eV. Oxidation resistant 25 cm long, 0.2 mm diameter alloy wires were used as a catalyzer. The wire was wound around the holder in a W-shaped

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http://dx.doi.org/10.1016/j.tsf.2014.10.022
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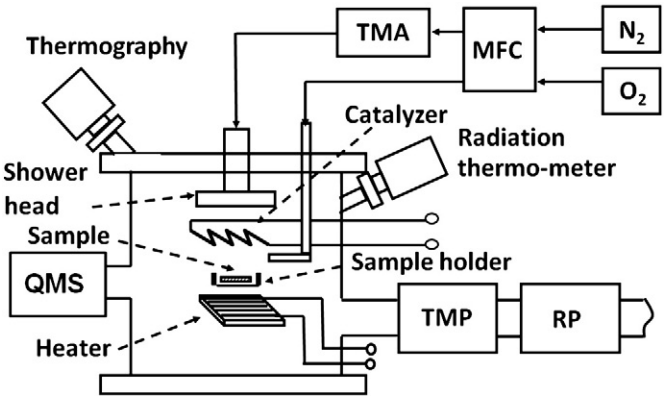


**Fig. 1.** Schematic illustration of apparatus used in this experiment.

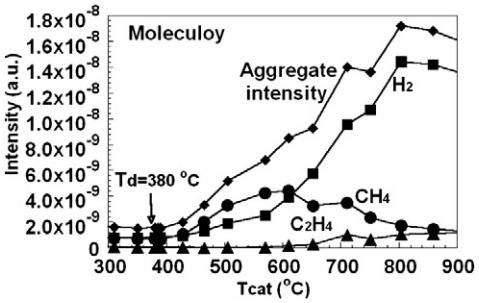


**Fig. 2.** Catalyzer temperature dependence of fragment intensities measured by QMS in TMA decomposition.

bend, and the catalyzer temperature ($T_{cat}$) was measured by a radiation thermometer. The decomposition of TMA was carried out at the TMA gas flow rate of 1 sccm and $N_2$ gas flow rate of 1 sccm as the carrier gas. The TMA gas was introduced through the shower head. The decomposition of TMA was carried out varying the catalyzer temperature in the range of 300 °C–900 °C under a chamber pressure of 50 Pa. The Si samples used as substrates in alumina formation were Czochralski (CZ) grown crystalline p-Si (100) wafers having a resistivity of 10 Ωcm with a mirror-polished front surface and a chemical-polished back surface. 2 cm × 2 cm samples were scribed from the wafer. The samples were slightly etched by a 2.5 wt.% hydrofluoric acid (HF) rinse to remove the natural oxide and to obtain an H-terminated surface, and rinsed in deionized (DI) water prior to deposition. The samples for deposition were mounted on the sample holder 7 cm away from the catalyzer. The samples were heated from the back side by radiation from a Chromel-wire heater mounted in a zigzag manner on a ceramic plate as shown in the figure. The sample temperature ($T_s$) was measured by thermography. Alumina films were prepared on p-type Si substrates by using $N_2$ gas as the carrier gas for the TMA. The mixture of TMA and $N_2$ was introduced through a shower head, while $O_2$ gas was

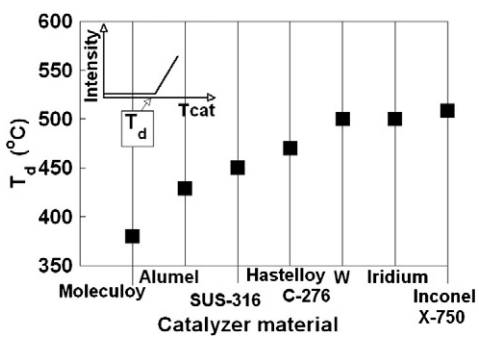


**Fig. 3.** Decomposition temperature in alloy materials used as catalyzers.

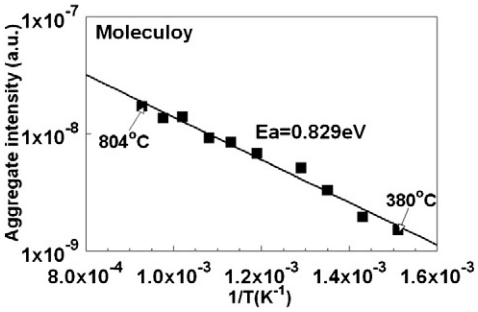


**Fig. 4.** Arrhenius plot of decomposition intensity of TMA in Moleculoy catalyzer.

independently blown around the catalyzer as shown in the figure. The substrate temperature ($T_{sub}$) was measured by a thermography. The films were prepared at $T_{sub}$ of 150 °C, $O_2$/TMA gas flow-rate ratio of 10 and $N_2$ gas flow-rate of 1 sccm at varying $T_{cat}$ in the range of 300 °C–900 °C. The alumina film thicknesses of the samples were measured by a spectroscopic ellipsometer (ALPHA-SE, J.A. Woollam Co. Inc.). Since the measured thickness included the natural oxide thickness, the actual thicknesses of the alumina films were determined by subtracting the natural oxide thickness of 1.16 nm from the measured thickness.

## 3. Results and discussion

The mass spectra for the various fragments resulting from the decomposition of TMA with various catalyzers were measured using QMS at varying catalyzer temperature in the range from 300 °C to 900 °C. The QMS spectrum intensities for the fragments such as $CH_4$, $H_2$ and $C_2H_4$ corresponding to the mass numbers of 16, 2, 28, respectively, were observed to be greater than some other negligibly small fragment intensities at $T_{cat}$ in the range of 300 °C–800 °C. However, Al fragment ions were not observed. It may be due to the fact that Al species could not arrive at the ionization-filaments which were set far away from the chamber wall. $CH_3$ fragment ion is also one of the good indices but we did not adopt it in this study since its fragment also includes $C_2H_6$ and $C_3H_8$. $CH_4$, $H_2$ and $C_2H_4$ fragment ions in the QMS measurements were the key fragment ions among other fragment ions in decomposition of TMA with the exception of $C_2H_4$ fragments which also included $N_2$ ions. Therefore, these three fragments were identified as indices to characterize the decomposition of TMA. The three fragment-ion intensities were corrected taking into the probability of ionization in QMS consideration and furthermore, $C_2H_4$ intensity was corrected by subtracting the $N_2$ ion component intensity. The three fragment intensities resulting from decomposition using Moleculoy as the catalyzer are shown as a function of catalyzer temperature in Fig. 2. As seen in this figure, the temperature at which the intensity of $CH_4$ fragments begins to rise was defined as the decomposition temperature ($T_d$) which is one of the indices for characterizing the

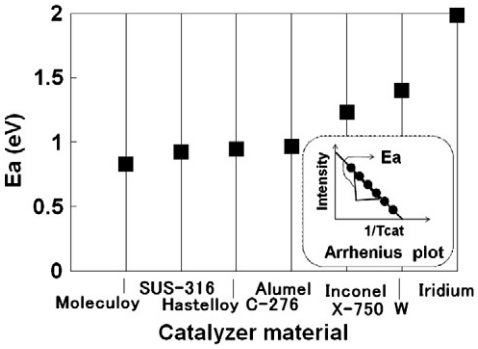


**Fig. 5.** Activation energy in alloy materials used as a catalyzer.