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CVD elaboration and *in situ* characterization of barium silicate thin films

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Abstract

This study is concerned with the elaboration of barium silicate thin films by metal organic chemical vapor deposition (MOCVD) and *in situ* characterization by X-ray photoemission spectroscopy (XPS) with an apparatus connected to the deposition reactor. The difficulty to find an efficient metal organic precursor for barium is described. After characterizations of the selected reactant, Ba(TMHD)$_2$tetraglyme, the development of an original specific vapor delivering source which allows reactant sublimation in the CVD reactor was performed. In the most optimized cases, including use of oxygen introduction during the deposition, barium silicate films were obtained. Moreover, non-negligible amounts of carbon and presence of barium oxide on the top of the layers were observed.

Keywords: Silicate; Barium; Films; Spectroscopy; Insulator

1. Introduction

The intense scale-down in integrated circuits (IC) metallization reveals the limits of SiO_2 as a gate insulator.[1] In order to find a replacement, some metal oxides were investigated.[1,2] Except for HfO_2,[3] their respective stabilities were not sufficient to fully satisfy the requirements of next generation electronic devices.[4,5] Among these disadvantages, formation of interfacial silicon oxide was found to attenuate dielectric properties.[1]

However, such an interfacial oxide formation may be exploited if it leads to a silicate material having high dielectric properties. Indeed, due to their dielectric properties[6] and chemical stability,[7] some silicates may belong to the next generation gate material. In this field, considering the high affinity of barium for oxygen, we choose to study the possible formation of barium silicates through reaction between this metal and silicon oxide substrate.

In a previous work,[8] the first steps of such a study have been presented. Metallic barium has been evaporated on silicon oxide films in order to study the reactivity of this system, with the help of core levels and valence band synchrotron-induced photoelectron spectroscopy (SP-PES) as well as transmission electron microscopy (TEM). It appears that deposited barium strongly reacts toward oxide substrate leading to oxidized barium species, and in appropriate conditions to the formation of barium silicates with a sharp interface with the substrate. Moreover, essential data concerning their binding energies have been obtained, and may be used in the continuation of this work.

Once barium silicates formation by interfacial silicon oxide consumption was demonstrated; the idea was to use a deposition way closer to industrial processes, i.e. CVD, and in particular, MOCVD. Hence, in this paper, we present the difficulty to find a metal organic precursor for barium CVD, the development of a specific adapted vapor delivering source as well as the first results concerning elaboration of barium silicates by CVD.

2. Precursor choice

A metal organic precursor which has to be used in CVD requires the following properties: good stability at room temperature and toward air, low vaporization or sublimation temperature, high vapor pressure and stability in vapor phase. The choice of a precursor for barium compound CVD film, allowing these properties, is a real challenge. Indeed, because of an unfavorable charge to diameter ratio of Ba^{2+} ion,[9] only two ligands can be added. Thus, saturation of central atom by ligands leading to vaporizable barium precursor is difficult. Moreover, oligomerisation of molecules can decrease the electron lack of barium central atom, through a multiplicity of ionic bindings with ligands, resulting in the decrease of sterical hindering and thus canceling the ligands' volatility. These reasons, added to the

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need of efficient precursors for microelectronic industry, explain the great ligand diversity developed for barium.[10]

Two main barium precursor families can be distinguished as function of fluorine presence in the ligand or not. Unfortunately, the use of fluorinated precursors mainly results in BaF_2 formation.[11] The layer treatment by water vapor used for the dissociation of such a compound generally induces rugosity and low-film density.[12] Fluorine containing precursors for barium are thus, not good candidates for ultra-thin film growth.

Among fluorine-free precursors, acetylacetonate compounds seem to be the most promising ones. In particular, the pentane-2,4-dione ligand (ACAC) is a possible candidate, through $Ba(ACAC)_2$ precursor. However, oligomerisation of this precursor induces sublimation temperatures above 200 °C and limits volatility.[11] Moreover, at these temperatures, precursor decomposition is too important to allow CVD use. To decrease the oligomerisation phenomenon, ligand sterical hindering increase is then an alternative. This could be carried out using 2,2,6,6-tetramethylheptane-3,5-dione ligand (TMHD), which is stabilized by four methyl groups.[11] The precursor is then the bis (2,2,6,6-tetramethylheptane-3,5-dionato) barium ($Ba(TMHD)_2$). It is a solid with sublimation temperature close to 190 °C.[13] Nevertheless, the oligomerisation phenomenon is not completely eliminated, and the single precursor can lead to tetramer $[Ba(TMHD)_2]_4$, having a vaporization temperature of 200 °C.[11] Moreover, the handling for introduction in the deposition device is delicate because of an significant sensitivity to air moisture.

Latest developments in barium metal organic precursors field consist in the addition of Lewis bases on existing precursors. The aim of these molecules is to increase the sterical hindering always, in order to produce stable monomer precursors with interesting sublimation temperature. Although Lewis bases addition improves water sensitivity and sublimation properties compared to $Ba(TMHD)_2$, dissociation possibilities during transport in the gaseous phase may persist.[14] However, for this purpose, numerous additions have been made, especially in amines and glycols ethers. Dialkyled glycol ethers are favored for our selection with the aim of avoiding any nitrogen pollution. The most hindering one has been chosen in order to provide sufficient sterical hindering: tetraglyme $CH_3O–(CH_2–CH_2–O)_4–CH_3$. The resulting precursor is $Ba(TMHD)_2$ tetraglyme (Fig. 1). It is a solid powder furnished by STREM Chemicals (Ba purity of 99.99%).

3. Precursor characterizations

Although TMHD ligand and $Ba(TMHD)_2$ precursor are well known,[15] few data concerning $Ba(TMHD)_2$ tetraglyme can be found in the literature. Indeed, this patented precursor is not commonly used and CVD barium films are often elaborated by techniques with less complicated precursors.[16,17,18] So, in this paragraph, results concerning stability of this precursor toward air moisture and temperature are presented.

It was found that tetraglyme addition to $Ba(TMHD)_2$ precursor results, among other things, in molecule stabilization toward humidity. Indeed, molecule hydrolysis was studied by attenuated total reflection infrared spectroscopy (Bruker IFS 28 equipped with Golden Gate ATR 10500). In particular, the –OH band around 3300 cm^{-1} was followed during air exposure. A very small increase in this feature was observed during the first five minutes indicating that hydrolysis is almost negligible. Actually, precursor hydrolysis is quite slow and can be followed during numerous hours. Moreover, no significant evolution is observed on the whole spectra during the first times of air exposure evidencing stability of the precursor. Hence, it was demonstrated that tetraglyme addition to $Ba(TMHD)_2$ precursor results in molecule stabilization toward humidity. This point is very crucial because it allows precursor introduction in MOCVD reactor without any special device.

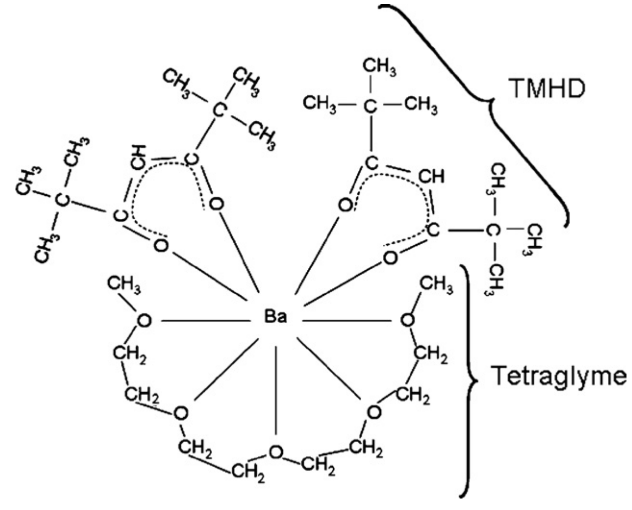

Fig. 1. $Ba(TMHD)_2$ tetraglyme formula.

Precursor behavior toward thermal treatment was studied by thermo gravimetric analysis with low pressure SETARAM balance (MTB 10.8) in order to characterize the sublimation temperature range. Two mass losses are observed (Fig. 2), between 40 and 75 °C, and between 230 and 280 °C, respectively. The first mass loss corresponds to approximately 30% of the total mass, while tetraglyme molecular weight (M = 222 g mol^{-1}) is equal to approximately 30% of the precursor total mass

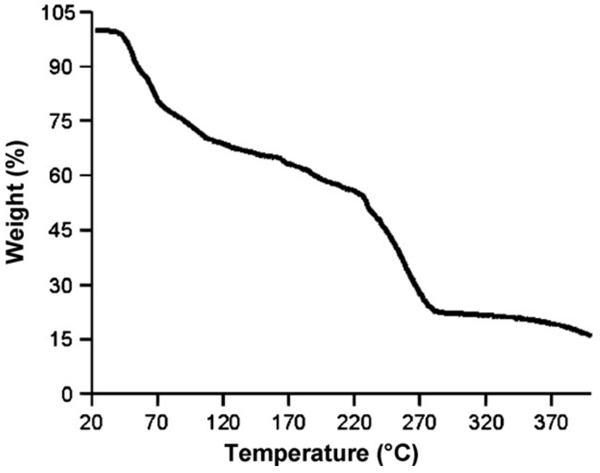

Fig. 2. $Ba(TMHD)_2$tetraglyme mass losses with 4×10^{-4} mbar low pressure.

($M = 725\,\mathrm{g\,mol^{-1}}$) too. Moreover, Inorowic et al.[19] observe the separation of tetraglyme molecule from the precursor in the approximately same temperature range. The first mass loss seems thus related to tetraglyme departure from molecule whereas the second mass loss can be attributed to Ba(TMHD)$_2$ sublimation.

These observations show that this precursor can be handled in air during short time without degradation. Moreover, total sublimation is possible, but at temperatures higher than 300 °C. So, a specific vapor precursor supply system has to be developed in order to satisfy these requirements.

4. Experimental set-up

The aims of this study are, on the one hand to elaborate CVD thin films of barium silicates for IC metallization, and on the other hand to characterize the obtained layers. It should be noticed that IC gate insulator thickness is very small, typically a few nanometers. Classical characterizations techniques such as X-ray diffraction are not well suited for studying objects at this length scale and the best is to carry out chemical characterizations to specify the compounds present in the layer. Electron spectroscopy such as XPS is well adapted for this kind of work because they allow not only obtaining elementary composition, but also piece of information about chemical bonding of different elements. However, thanks to the small thickness of studied layers which is of the same order of magnitude as the pollution layer thickness linked to air exposure and as the information depth of this technique, *in situ* characterization is really essential. In order to allow CVD elaboration and electron spectroscopy characterization without air contamination, an original set-up has been developed.[20] The set-up, composed of two specific chambers, is completely built up with ultra high vacuum technology and introduction of samples is ensured by a rapid introduction small volume chamber.

The first chamber is dedicated to analyses. It is equipped with one double anode X-ray source (Al Kα and Mg Kα) and one monochromatized Al Kα source. Electron detection is provided by a hemispheric analyzer CLAM 4 MCD (Thermo VG Scientific). Moreover, thanks to a high precision manipulator, it is possible to modify the photoelectron detection angle. In this way, this device is well adapted for XPS (X-ray Photoelectron Spectroscopy), but also Angle Resolved XPS (ARXPS) which can give in-depth information, and, after data treatment, thickness and surface coverage of deposited film.[21]

The second specific chamber is a horizontal CVD reactor, composed of quartz cylindrical tube linked to steal connections, with possibility to obtain ultra high vacuum, by means of turbomolecular pump allowing transfer in analysis chamber. Heating is provided by an induction furnace CELES GTM 3 (3 kW, 100/300 kHz), controlled by a thermocouple connected to the sample holder. This kind of heater allows a limitation of the reaction zone to the substrate holder only, leading to a cold wall reactor and a limitation of gaseous phase reaction.

For this work, a specific vapor delivering source has been developed. Indeed, we have shown in the part dedicated to the precursor choice, that Ba(TMHD)$_2$tetraglyme is the best compromise for MOCVD barium compounds, considering our constraints. But, this molecule needs some caution for manipulating. In particular, precursor vapor production and transport are estimated to take place at temperatures around 200 °C. So, vapor delivering source exterior to the deposition system is not realistic, because it would require maintaining the source, but also the complete gas line and the income in the reactor, at the desired temperature. These points are incompatible with ultra high vacuum device, and a vapor delivering source composed of a sublimation system integrated to the reactor was chosen. Moreover, as vapor phase stability was not known, it was necessary to reduce as much as possible the transport distance. It results in precursor sublimation near the reaction zone. In this way, an original and simple vapor delivering source was developed. An oven containing the precursor powder was added on the rod of the substrate handler, this oven being mobile in regard to the handler thanks to a magnetic translation system present inside the rod. The oven, temperature of which is controlled by thermocouple, is heated by inductive coupling of the induction furnace. Thus, by moving the oven position, precursor temperature can be easily changed while maintaining the proximity between the source and the substrate. With this system, the precursor can be heated up to 280 °C, for substrate temperatures ranging between 500 and 700 °C.

5. CVD growth and *in situ* characterization

The growths were performed on (1 0 0) oriented n-type silicon substrates, polished on one side. Prior to the deposition process, each wafer was chemically cleaned. It was dipped for 5 min in H_2SO_4:H_2O_2:H_2O (6:1:1), rinsed with deionised water, dipped for 10 s in HF:H_2O (10% diluted), rinsed with deionised water again, dried under N_2 blow and immediately introduced into the UHV system through fast-entry. This way of wafer preparation is known to remove native silicon oxide and to give rise to hydrogen terminated surface.[20] During the deposition within the previously presented reactor, the total pressure was fixed at 1.5×10^{-5} mbar, the precursor oven temperature was maintained around 120 °C, and the substrate temperature was ranking between 500 and 700 °C. The effect of oxygen introduction on the obtained layers was studied as well.

Concerning the XPS experiments, data were treated with the CasaXPS software package. All spectra were referenced to the metallic Si^0 $2p_{3/2}$ peak positioned at 99.3 eV.[22] Moreover, the extremely low thickness of the layers makes quantification by correcting peak area with sensitivity factors very difficult. For this reason, in this work, only elements area ratio evolutions are presented.

The same kind of survey XPS spectra were obtained (Fig. 3), whatever the deposition conditions are. XPS and Auger signals corresponding to barium, oxygen, carbon and silicon are identified. A high carbon amount is always observed which could not be linked to pollution related to air exposure because experiments are here performed *in situ*. Nevertheless, higher resolution observation of different characteristic lines allows getting more information, in particular as function of the deposition temper-

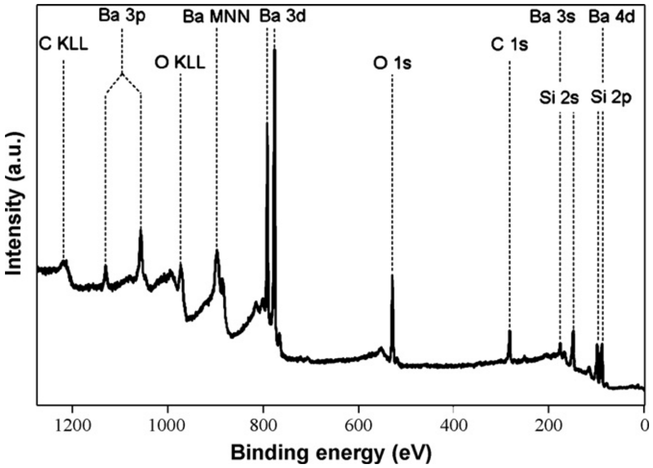

Fig. 3. Characteristic broad XPS survey spectrum.

ature. In Fig. 4 are presented the Ba 4d, O 1s and Si 2p lines for three different growth temperatures without oxygen introduction in the three bottom curves. It is clear in the Ba 4d region that, although the global area of the peak increases with increasing temperature, no significant difference is evidenced, and in the observed energy positions which are intermediate between the ones of barium oxide and silicate.[8] The most interesting information is given by O 1s and Si 2p regions. Two contributions can be observed in O 1s line: one at 528 eV corresponding to barium oxide and one at 530 eV which could correspond to barium silicate.[8] In parallel, in the Si 2p line two contributions can be evidenced: in addition to the Si^0 one, a feature at 102.0 eV can be revealed for growth at 700 °C. Such a peak cannot be attributed to SiO_2 and its binding energy is consistent with the one of silicate component.[8] Thus, these deposition conditions allow both oxide and silicate growths, the temperature influencing their respective amount. Limited thickness of the deposited layer is confirmed by the presence of Si^0 metallic contribution in Si 2p region. Through the modeling of the attenuation of Si^0 signal, thickness is evaluated to be close to 3 nm. At last, C 1s line (not shown here) does not give more information. Only one component is present, always at the same binding energy (approximately 284.5 eV), attributed to carbonaceous species coming from the incomplete decomposition of the precursor.

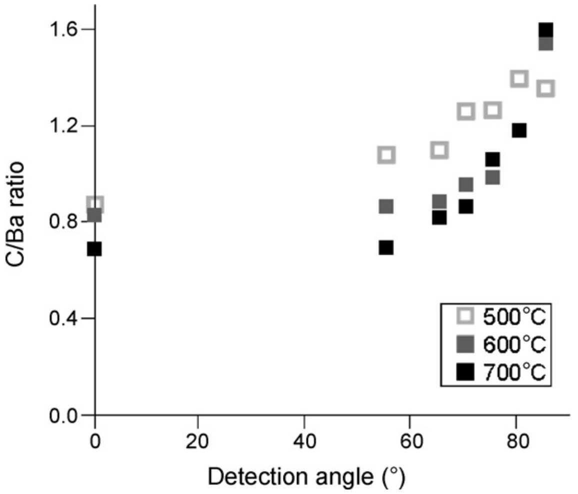

Fig. 5. Evolution of the carbon to barium amount in function of deposition temperature and photoelectron detection angle with respect to the surface normal.

Evolutions of the ratio of the carbon to barium peak areas as function of detection angle for different deposition temperatures are presented in Fig. 5. The smallest ratio is obtained at 700 °C, using the smallest photoelectron detection angles with respect to the surface. This evolution signifies that carbon is rather located in the superficial layer and its amount decreases with deposition temperature. These behaviors can be explained by a growth limited by the precursor carbonaceous sub-products desorption.

The effect of oxygen introduction on the silicate formation has been also studied. The binding energies corresponding to the different elements are not modified (Fig. 4). The main result is the decrease of the carbon to barium ratio with the increase of oxygen pressure. However, ARXPS study shows that barium remains located in the interfacial layer.

At last, for sample obtained with the highest temperature and oxygen pressure (700 °C and 2×10^{-6} mbar), corresponding to the most interesting deposition conditions, the in-depth repartition of the different species, barium oxide and silicate, was studied (Fig. 6) through the evolution of the O 1s line. Indeed, as it was said previously underlined, O 1s line reveals the presence of both silicate at 530 eV and of oxide at 528 eV. It is clearly observed that relative contribution of silicate decreases at

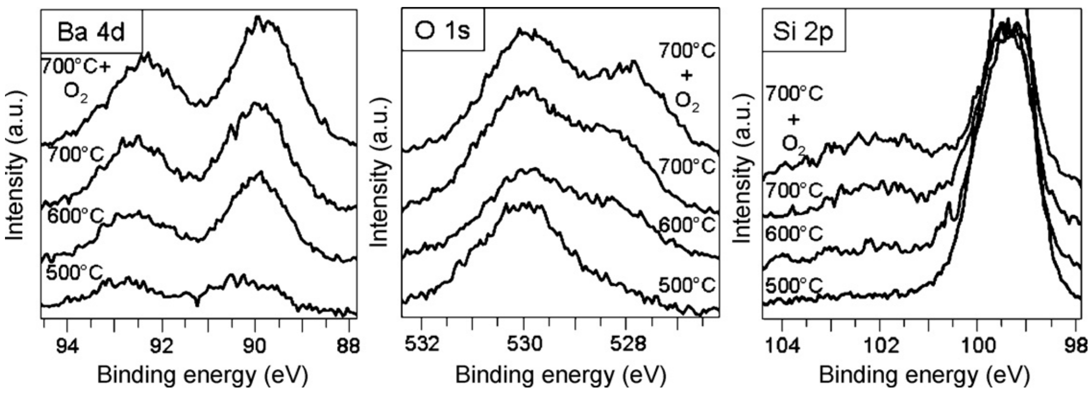

Fig. 4. Ba 4d, O 1s and Si 2p XPS lines, for growth temperatures of 500, 600 and 700 °C without oxygen introduction; and 700 °C with 2×10^{-6} mbar oxygen pressure.

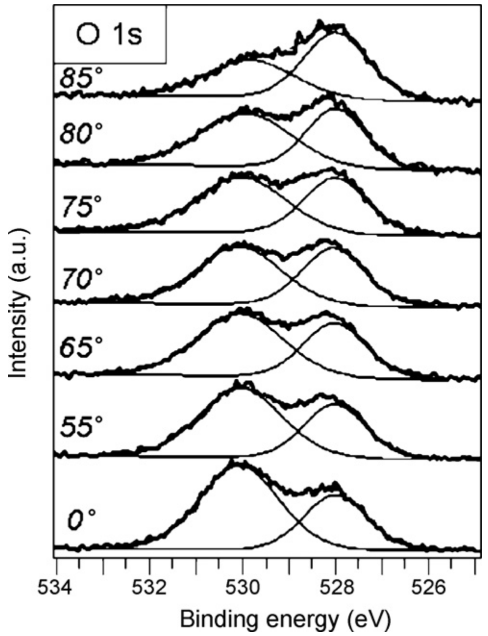

Fig. 6. O 1s XPS line in function of photoelectron detection angle with respect to the surface normal, for a film obtained at 700 °C with 2×10^{-6} mbar oxygen pressure.

increasing detection angles while oxide contribution increases. It means that the oxide is more present on the top of the layer whereas silicate is located at the interface. In Si 2p line not shown here the metallic contribution disappears when the detection angle increases, while the silicate contribution is quasi-constant.

6. Conclusion

In this study, barium silicate thin films were elaborated by MOCVD and characterized *in situ* by XPS and ARXPS, in the same specific set-up. Difficulty to find a metal organic precursor for barium CVD was shown: it is essentially due to oligomerisation phenomenon because of a lack of central atom saturation by ligands. However, a solution was found through the use of an acetylcetonate, Ba(TMHD)$_2$, with tetraglyme Lewis base addition. For this precursor, stability toward air moisture and sublimation possibility were demonstrated. A specific vapor delivering source was thus developed, allowing reactant sublimation close to the substrate in the CVD reactor at a desired temperature. In this way, problems related to transport phenomena are limited. In these conditions, first deposits were obtained, with thicknesses estimated to 3 nm. With the best used conditions, i.e. 700 °C as deposition temperature and oxygen pressure of 2×10^{-6} mbar, barium silicate film was formed, located at the substrate interface. In addition barium oxide is always present on the top of the layer. Moreover, with these conditions, carbon incorporation in the layers is minimized, but still present linked to incomplete decomposition of precursor. In order to solve this problem, deposition conditions, precursor oven temperature in particular, will be optimized with the aim to both decrease the carbon amount in the layer and to obtain homogeneous barium silicate single layer.

This work opens lots of perspectives. First of all, transmission electron microscopy analyses are planned in order to observe the layer morphologies (good conformity, in-depth homogeneity, . . .). Electrical analyses are in progress with the aim to confirm the interest of this material for gate insulator applications.

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