● Ruthenium / Cobalt Precursors for Area-Selective Deposition

Advanced Materials Research Laboratory, Advanced Integration Research Center, TOSOH Corporation

Kohei Iwanaga
Ryosuke Ebihara
Shuya Ikemura
Hiroyuki Oike

1. Introduction

In recent years, as electronic devices have become increasingly miniaturized, chemical vapor deposition (CVD) and atomic layer deposition (ALD) methods have become increasingly important as they can deposit ultra-thin films in a limited space. CVD and ALD vaporize volatile metal precursors and deposit films via chemical decomposition in a deposition chamber. While industrially well-known halides and alkoxides have been commonly utilized as precursors, they are no longer able to meet all of the requirements of state-of-the-art device manufacturing processes.

In order to provide solutions to such high-level requirements of next-generation semiconductors, the introduction of new compounds has been extensively investigated.[1] Such new precursors satisfy a variety of properties desirable for CVD/ALD processes: good vaporization properties, low melting points, thermal stability, proper chemical reaction properties, etc.

While device microstructures require deposition accuracies of single-digit nanometers or less, area selective deposition (ASD) has been intensively investigated as an alternative to physical lithography as a means of efficient microstructure formation.[2] ASD enables the formation of a desired film in one area while suppressing deposition in adjacent areas, depending on the pattern of the substrate surface. ASD not only makes the device fabrication process more efficient, but also reduces the consumption of raw materials and energy used in the process.

Typically, an ASD process is achieved by a combination of several techniques. (**Fig. 1**) For example, by depositing inhibitor on the substrate surface, the adsorption of precursor on the substrate surface can be passivated. In other cases, a small amount of metal deposited on the undesired surface can be removed by the etch-back process.

However, these techniques complicate the process and deteriorate material and energy efficiency. Intrinsic area-selective adsorption properties of the precursor would make the process more efficient. Such precursors have been intensively studied, but there are few reports of compounds which have a desirable combination of adsorption properties and sufficient selectivity.[3]

We have developed a series of oxide, metal, and low-k precursors for CVD/ALD. In this technical document, we review the excellent intrinsic area selectivity of cobalt precursor Ts-Co10 [4] and ruthenium precursor Rudense (ref 4)[5], precursors for metal thin
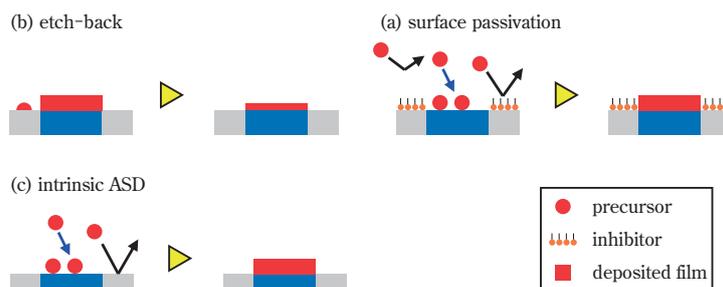
Fig. 1　Typical techniques used for ASD processes

film deposition.[6] We believe that our developments will contribute to the implementation of next-generation semiconductor devices utilizing area selective deposition and to the reduction of environmental impact through more efficient device fabrication.

2. Basic Properties of the precursors

The basic properties of Ts-Co10 and Rudense are summarized in **Table 1**. Both precursors are liquid at around room temperature. Their vapor pressures are high enough (**Fig. 2**) to be supplied to the deposition chamber by the bubbling method.

Thermogravimetric analysis (TG) and differential scanning calorimetry analysis (DSC) were measured as thermal analysis.

TG [7] (**Fig. 3**) shows that they have good vaporization properties without residue. DSC[8] (**Fig. 4**) was used to measure their thermal decomposition temperatures (T_{dec}): T_{dec} of Ts-Co10 is 210℃, which is thermally stable

Table 1　Basic properties of the precursors

	Ts-Co10	Rudense
Appearance		
melting point	< 20℃	< 27℃
vapor pressure	0.1 Torr @88℃	0.1 Torr @76℃
T_{dec}	210℃	230℃
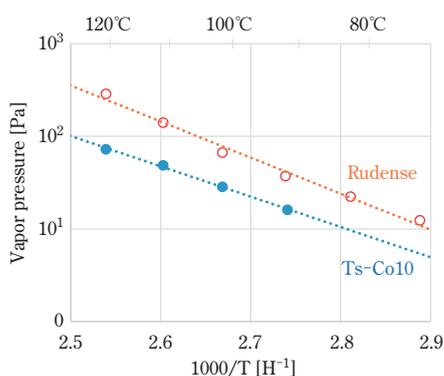
Fig. 2　Vapor pressure of the precursors

(Ar flow: 400 mL/min, heating rate: 10℃/min)
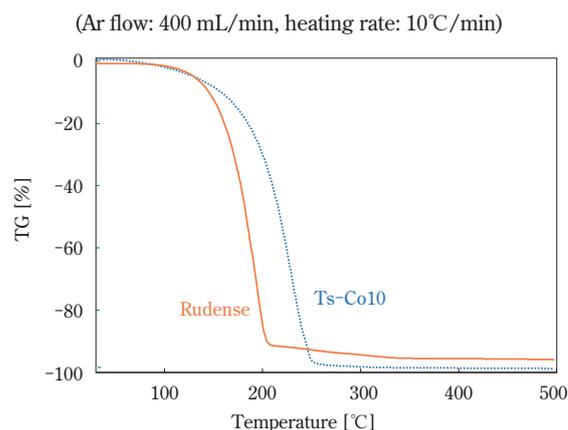
Fig. 3　TG curves of the precursors

(Sealed under Ar, heating rate: 10℃/min)
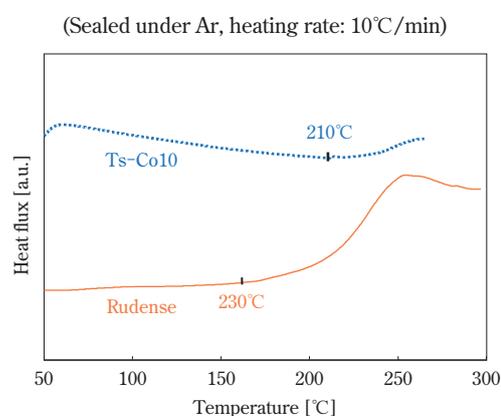
Fig. 4　DSC curves of the precursors

for a cobalt complex. T_{dec} of Rudense is 230℃, which also shows sufficient thermal stability.

3. CVD Deposition Test and their ASD Properties

ASD properties of Ts-Co10 and Rudense were evaluated by CVD method. The deposition apparatus was illustrated in **Fig. 5**. The precursors were vaporized by a bubbling method, and the vapors were transferred to deposition chamber using argon (Ar) as a carrier gas. Ar is also used for a diluent. Reactant gases were selected from ammonia, hydrogen, and formic acid. Formic acid was vaporized by a bubbling method. The thickness of deposited films were estimated by the X-ray fluorescence (XRF) calibrated by standard samples.

3.1 Ts-Co10

Fig. 6 shows the cobalt film thickness versus deposition time plots on a series of substrates (Ru, Pt,
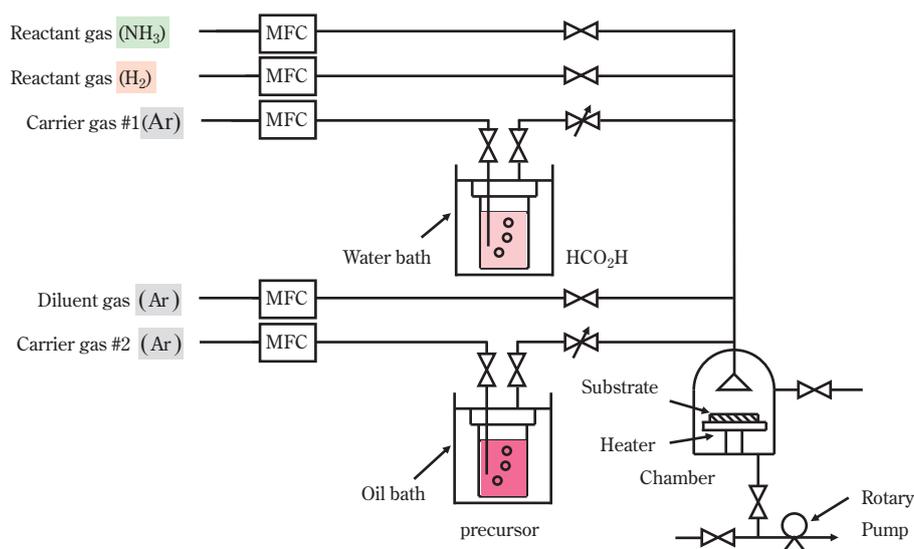
Fig. 5　CVD apparatus
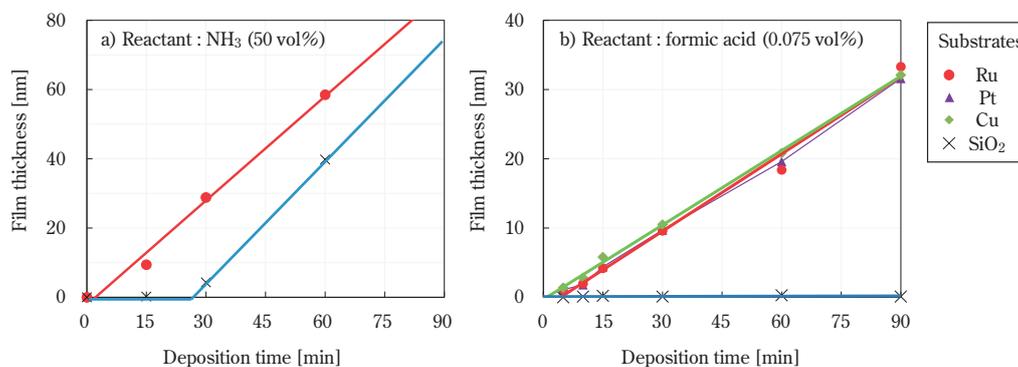
Fig. 6　Deposition time dependency of CVD with Ts-Co10 (Depo. Temp. : 200℃)

Cu, and SiO_2.) When using ammonia as a reactant gas, longer incubation time was observed on SiO_2 substrate than on Ru, which indicates the nucleation delay on SiO_2 substrate (**Fig. 6**a). Interestingly, using a small amount of formic acid as a reactant gas improves Ts-Co10's metal-on-metal area selectivity, and the cobalt film formation was achieved on Ru, Pt, and Cu substrates while there is no film on SiO_2 substrate after 90 minutes of deposition process (**Fig. 6**b). Surface SEM images also show deposition according to film thickness, and nucleation is suppressed on the SiO_2 substrate, and furthermore, there was no nucleation observed when formic acid is used as a reactant (**Fig. 7**). We also confirmed that high area selectivity is maintained at 150-250℃ using Ts-Co10 and formic acid (**Fig. 8**.)
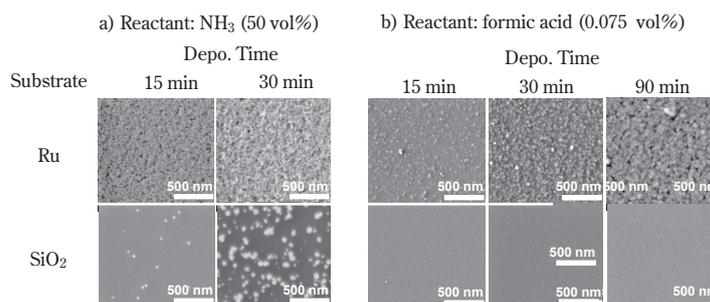
Fig. 7　Surface SEM images of deposited substrates plotted in Fig. 6
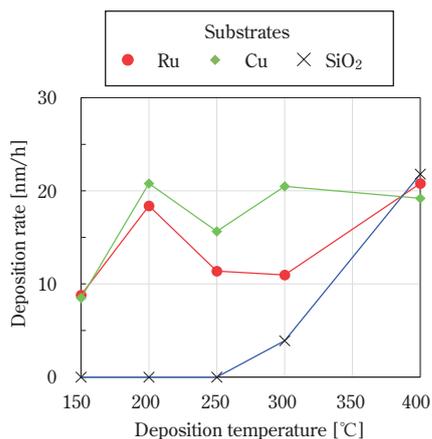
Fig. 8 Deposition temperature dependency of CVD with Ts-Co10 (Depo. Time: 60 min)
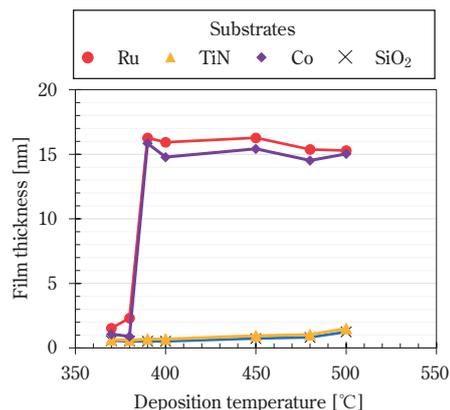
Fig. 9 Deposition temperature dependency of CVD with Rudense

(Depo. Time: 30 min, NH_3/H_2 ratio: 70/30)

3.2 Rudense

Rudense can form pure ruthenium thin film by CVD process using ammonia as a reactant gas, and interestingly, ammonia/hydrogen mixed reactant gas improves the deposition rate and reproducibility. Temperature dependency plot (**Fig.9**) shows Rudense's area selective deposition nature, which can form thin films on Ru and Co surface while the film deposition on SiO_2 and TiN is suppressed. At 400℃, no film was observed on SiO_2 and TiN substrates after 120 min of deposition (**Fig. 10**) while there was linear film growth on Ru and Co substrates. The suppression of film formation was also confirmed by cross-sectional TEM images (**Fig. 11**), and a small amount of grains of about 1 nm were observed.
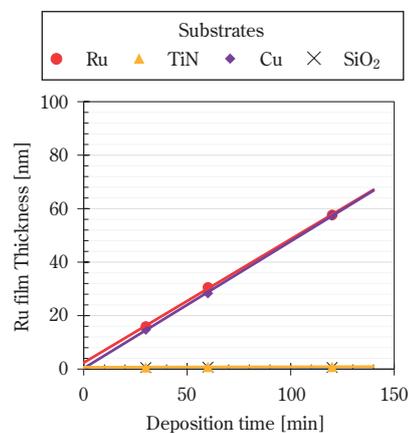
Fig.10 Deposition time dependency of CVD with Rudense

(Depo. temp: 400℃, NH_3/H_2 ratio: 70/30)
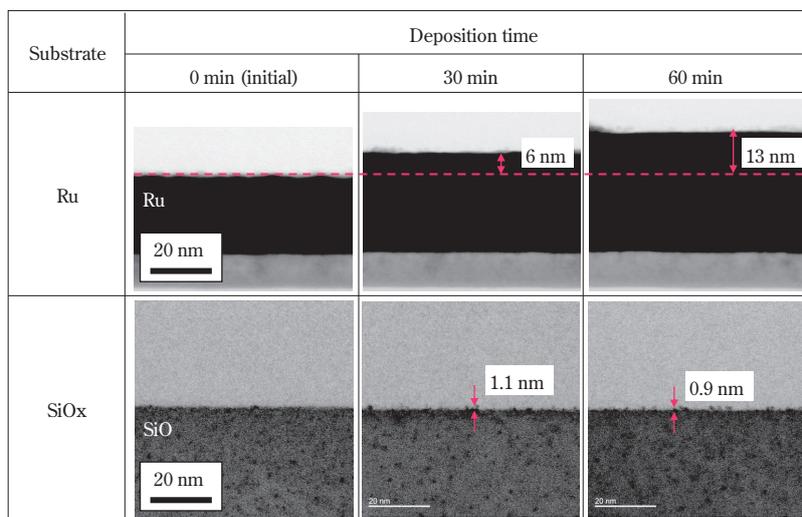
Fig.11 Cross-sectional TEM images

4.　Summary and Perspectives

Our precursors, Ts-Co10 and Rudense, are summarized with their basic properties and area selective deposition characteristics for CVD. Both precursors exhibit excellent metal-on-metal ASD properties, which enables film formation on metal substrates while inhibiting the deposition on dielectrics such as SiO_x. We are currently developing the application of these precursors into a Ru and Co thin film formation processes. We are also currently working on optimizing molecular design and deposition conditions to achieve, for example, lower deposition temperature and improved selectivity to a wider range of substrates.

5.　Acknowledgements

6.　References

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6　A part of this report includes the content of the presentation at ADMETA Plus 32nd Asian Session : K. Iwanaga, T. Hayakawa, Y. Yamamoto, H. Oike, R. Ebihara, and K. Tada, *ADMETA Plus 32nd Asian Session*, S5-2(2023)

7　TG analyses were carried out under an Ar flow (400 mL/min) at a heating rate of 10 ℃/min with a SII Technology TG/DTA7200 that was contained in a nitrogen-filled glovebox to prevent decomposition arising from exposure to air.

8　DSC was performed using a SII Technology DSC7020 at a heating rate of 10 ℃/min with a sealed container in an Ar gas atmosphere.