Purification of Hafnium by Hydrogen Plasma Arc Melting

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1. Introduction

The interests in refractory metals, their alloys and compounds have been raised from the needs in the advanced technology fields. Recently, refractory metal oxides such as HfO$_2$ and ZrO$_2$ have been reported to be a promising candidate for high-K gate insulator films for the fabrication of scaled-down metal-oxide-semiconductor field effect transistor (MOS-FET) devices, due to their high dielectric constants and thermodynamic high stability on Si surface. Then, high purity Hf metal as a sputtering target material will be required to improve the reliability and the lifetime of devices. For instance, some trace impurities may cause an increase in the gate leakage current, due to those oxides in HfO$_2$ being reduced to metals by Si. Therefore, it will become a very important subject to lower those impurity levels as low as possible.

By the way, Hf has a very high neutron absorption cross section, so its major use as metal is for the control rods in nuclear reactors. Besides, Hf is used as an alloying element for supper alloys and refractory alloys. Under the circumstances, high purity Hf has not been needed for the application until now and purification of Hf has not been studied so seriously.

As purification methods of sponge Hf produced by the Kroll process, fused salt electrolytic refining, iodide decomposition refining (Van Arkel process) and electron beam melting (EBM) have been known. Fused salt electrorefining in a bath of molten alkaline chlorides is an available process to prepare a high purity Hf with low nitrogen, but it is difficult to operate for refining of Hf on a large scale and then has not yet to be applied practically. On the other hand, the iodide process and EBM are commercially used for purification of Hf. EBM in high vacuum is well known as a practical and useful melting method for various metals and alloys. In most cases, Ar is used as a plasma generating gas and, in that case, the significant refining effect cannot be expected. It has been found, however, that an addition of H$_2$ to the plasma gas enhances the removal of non-metallic impurities such as O and N from Fe, Co and Ta and, furthermore, the removal of many metallic impurities from the melted refractory metals such as Zr, Nb and Ta. This H$_2$+Ar plasma arc melting is called “Hydrogen Plasma Arc Melting (HPAM)”.

We have already reported that HPAM is available for refining of Hf and, in the present work, we melted and refined two kinds of Hf metal with different purity by hydrogen plasma arc and investigated more concretely the reduction behaviors of many impurities in Hf with HPAM. In addition, in order to clarify the refining mechanism, the influence of the hydrogen content of plasma arc on the reduction rates of some metallic impurities was studied by using a Hf-base dilute alloy as the starting material for HPAM.

2. Experimental Procedure

2.1 Starting material

Two kinds of commercial Hf metal with different purity, a high-purity Hf (about 99.7% Hf in purity certified by the supplier, hereinafter abbreviated as “HP-Hf”) and a low-purity Hf (about 98% Hf in purity certified by the supplier, hereinafter abbreviated as “LP-Hf”) were used as the starting...
materials. Table 1 indicates the main impurity concentrations of both starting Hf, analyzed by GDMS.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>LP-Hf (mass ppm)</th>
<th>HP-Hf (mass ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1</td>
<td>0.02</td>
</tr>
<tr>
<td>Al</td>
<td>270</td>
<td>33</td>
</tr>
<tr>
<td>Si</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>P</td>
<td>2</td>
<td>0.06</td>
</tr>
<tr>
<td>S</td>
<td>2</td>
<td>0.4</td>
</tr>
<tr>
<td>Ti</td>
<td>31</td>
<td>18</td>
</tr>
<tr>
<td>V</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Cr</td>
<td>27</td>
<td>4</td>
</tr>
<tr>
<td>Mn</td>
<td>8</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>528</td>
<td>35</td>
</tr>
<tr>
<td>Co</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>Ni</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Cu</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>Zn</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Se</td>
<td>0.06</td>
<td>0.1</td>
</tr>
<tr>
<td>Mo</td>
<td>0.4</td>
<td>1</td>
</tr>
<tr>
<td>Sn</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>W</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>Zr (mass%)</td>
<td>1.2</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Total Impurity (except for Zr,C,N,O) 885 mass ppm ~100 mass ppm

Hf-Purity (except C,N,O) 98.7 mass% 99.5 mass%

arc furnace used in this work. The plasma torch is a d.c. arc discharged type with a maximum power of 20 kW. Each specimen (about 20 g) was placed on the water-cooled copper crucible with 60 mm in diameter and 5 mm in depth and melted for 10 to 60 min by Ar and H₂ (5, 10 and 20 vol%)+Ar plasma arc heating under atmospheric pressure. The power of plasma arc was set to be about 5.2 kW. The specimen after the first melting was melted again for the same time after turning it upside down for melting and refining it uniformly. Then, the melting time was a sum of the both time. The flow rate of the plasma generating gas introduced to the plasma torch was constant to be 5 dm³/min.

The impurity concentrations in Hf before and after plasma arc melting were determined by Glow Discharge Mass Spectrometer (GDMS, VG-9000). Also, the hydrogen content in Hf was analyzed by Ar gas fusion–thermal conductivity method using Horiba-EMGA 621.

3. Results and Discussion

3.1 Plasma arc melting and refining of HP-Hf

Figure 2 shows the changes of Fe, Cr and Ti concentrations in the HP-Hf melted by Ar and hydrogen plasma arc (5 to 20 vol% H₂) as a function of time. Compared with the case of Ar plasma arc melting, Fe, Cr and Ti were reduced more rapidly in the case of HPAM. In addition, those reduction rates increased with the hydrogen content of plasma gas and Fe and Cr decreased from 35 to less than 0.1 mass ppm and from above 1 to below 0.01 mass ppm, respectively, after 60 min of 20%H₂+Ar plasma arc melting. On the other hand, the removal of Ti had been supposed to be difficult because of Ti belonging to the same group of Hf, but Ti was removed slowly from about 20 to less than 5 mass ppm.

In regard to the other impurities in the HP-Hf, they were also removed like Fe and Cr, as shown in Fig. 3 and Table 2. This figure displays the concentration changes of a lot of impurities in the HP-Hf melted with 20%H₂+Ar plasma arc. Almost all impurities were reduced and it is found that the relatively more volatile impurities such as Fe, Al, Cr and Ni were removed more quickly from above 1 mass ppm to below
In addition, Mn, Mg, Sn and Cu, initially below 1 mass ppm, were further reduced to the lower levels. On the other hand, as presented in Table 2, no reduction of Zr and W, having vapor pressures close to that of Hf, was observed. From these results, the total impurity concentration of Hf, except for Zr, C, O and N, was decreased from nearly 100 to 5 mass ppm after 60 min of 20%H₂+Ar plasma arc melting, as shown in Table 2. Then, the purity of Hf, except for Zr, O, C and N, increased from 99.99 to more than 99.999 mass%. Then, it has been recognized that HPAM is very available for purification of Hf, i.e. elimination of various volatile impurities in Hf to the very low levels.

On the other hand, an increase in the hydrogen content of Hf during the HPAM treatment should be taken into consideration. In fact, for example, the hydrogen content of HP-Hf increased to about 90 mass ppm after 10 min of 20%H₂+Ar plasma arc melting. However, the increased hydrogen in Hf was able to be easily reduced to less than 1 mass ppm by 10 min of Ar plasma arc melting.

By the way, the mass loss of the melted specimens, caused by evaporation of Hf and impurities, during 60 min of 20H₂+Ar plasma arc melting was low to be nearly 1%. Then, the evaporation loss of Hf was very small and the recovery of Hf was high to be more than 99%, notwithstanding the excellent removal of various impurities during HPAM.

### 3.2 Plasma arc melting and refining of LP-Hf

Figure 4 shows the concentration changes of six impurity elements (Al, Fe, Cr, Ti, Sn and Mg) of LP-Hf with the Ar and 20%H₂+Ar plasma arc melting as a function of time. For Al, Fe and Cr with high concentrations in the starting LP-Hf, they decreased slowly by Ar plasma arc melting. However, their reduction rates were remarkably enhanced in the case of 20%H₂+Ar plasma arc melting and Al, Fe and Cr were efficiently reduced from over 100 to below 0.1 mass ppm, from about 500 to below 5 mass ppm and from above 10 to less than 0.01 mass ppm, respectively. Also, Sn and Mg with less than 1 mass ppm in the starting LP-Hf further decreased to below 0.1 mass ppm. On the other hand, Ti were scarcely reduced in Ar plasma arc melting but surely decreased from 18 to 3 mass ppm by 20%H₂+Ar plasma arc melting.

For the other impurities, as indicated in Table 3, almost all impurities (Ni, Mn, Cu, Co etc.) with higher vapor pressures
than that of Hf were reduced during 20%H$_2$+Ar plasma arc melting, but Zr and W were not reduced like the case of HP-Hf. Then, the total impurity concentration of LP-Hf, except for Zr, C, O and N, decreased from about 900 to below 20 mass ppm after 60 min of 20%H$_2$+Ar plasma arc melting, so the purity of LP-Hf, except for Zr, O, C and N, increased from 99.9 to about 99.998 mass%, as shown at the bottom line of Table 3. This result suggests that a high-purity Hf with
more than 99.999 mass% could be obtained even from the LP-Hf when the melting time was further increased.

Compared with the refining result reported for EBM of a sponge Hf by the Kroll method, in which any metallic impurities of Fe, Al, Cu and Ti could not be reduced to less than 10 mass ppm,\textsuperscript{3,5)} the purification result of HPAM in this work is recognized to be superior to that of EBM, because those impurities were reduced quickly to the considerably lower levels during HPAM. Then, HPAM is concluded to be a very useful purification method for Hf.

3.3 Influence of the hydrogen content of plasma arc on the refining effect

In order to examine an influence of the hydrogen content on the reduction rates of several metallic impurities, HPAM of a Hf-base dilute alloy, about 20 g in weight, containing each 0.1 mass% of Al, Cr, Cu, Fe and Ti (totally 0.5 mass% in five impurity elements added altogether), which was prepared by the addition of them to the HP-Hf followed by melted with Ar plasma arc, was carried out and the removal behaviors of them were investigated as a function of the hydrogen content.

Figure 5 represents the concentration changes of Al and Ti in the Hf-base dilute alloy melted by 5, 10 and 20%H\textsubscript{2}+Ar plasma arc, as a function of melting time. The reduction of Al and Ti were enhanced with increasing the hydrogen content of plasma gas and, in this figure, the relationships between the Fe and Al concentrations in logarithm and the melting time became almost linear at each hydrogen content. For the case of Fe, Cr and Cu, the same tendencies were observed. These results mean that the removal and vaporization of those metallic impurities from the Hf-melt during HPAM obeys a first-order rate law.

For an example, the removal of Al can be expressed by eq. (1), in which [%Al] and \(k_{\text{Al}}\) are the Al concentration in mass% and the apparent reduction rate constant of Al, respectively. Integration of eq. (1) gives eq. (2), [%Al\textsubscript{0}] and [%Al\textsubscript{t}] mean the Al concentration at \(t = 0\) and \(t = t\), respectively. The \(k_{\text{Al}}\) at the respective hydrogen content of plasma gas can be derived from the slopes of the straight lines in Fig. 5(a), according to eq. (2). Also, the \(k\) values of Ti, Fe, Cr and Cu at 5, 10 and 20%H\textsubscript{2}+Ar plasma arc melting are obtained in the same way.

\textbf{Fig. 5} Changes in the Al and Ti concentration of the Hf-base dilute alloy, initially containing each 0.1 mass% of Al, Cr, Cu, Fe and Ti, during 5 to 20%\textsubscript{2}+Ar plasma arc melting.

\textbf{Fig. 6} Dependence of the apparent reduction rate constant (\(k\)) of Al, Ti, Fe, Cr and Cu on the hydrogen content (%H\textsubscript{2}) of plasma arc during HPAM of the Hf-base dilute alloy.

\[
- \frac{d[\%\text{Al}]}{dt} = k_{\text{Al}}[\%\text{Al}]
\]

\[
\log[\%\text{Al}\textsubscript{0}] - \log[\%\text{Al}\textsubscript{t}] = k_{\text{Al}} t/2.303
\]

Next, the apparent reduction rate constants (\(k\)) of Al, Ti, Fe, Cr and Cu are plotted against the hydrogen content (%H\textsubscript{2}) in log-log scale, as shown in Fig. 6. The relationships between \(k\) and (%H\textsubscript{2}) are observed to be linear in this figure and, as an example, the slope of \(k_{\text{Al}}\) against (%H\textsubscript{2}) is calculated to be about 0.8, which becomes to eq. (3a) and (3b). By substituting eq. (3b) into eq. (1), eq. (4) is obtained. Equation (4) suggests that the reduction (removal) rate of Al increases proportionally to about 0.8th power of the hydrogen content of the plasma gas.

\[
k_{\text{Al}} \propto (\%\text{H}_2)^{0.8}
\]

\[
k_{\text{Al}} = k_{\text{Al}}^{(\%\text{H}_2)^{0.8}}
\]

\[
- \frac{d[\%\text{Al}]}{dt} = k_{\text{Al}}^{(\%\text{H}_2)^{0.8}}[\%\text{Al}]
\]

From Fig. 6, the reduction rates of Ti, Fe, Cr and Cu are also found to increase proportionally to about 0.9, 0.6, 0.5 and 0.5th power of the hydrogen content, respectively. Therefore, the metallic impurities with higher vapor pressures than that of Hf can be removed according to eq. (5), and there is some difference in the dependence of vaporization rate of each impurity element on the hydrogen content of plasma arc.
by hydrogen atoms are considered. Important role. Concretely, the following processes caused formed in the high temperature plasma arc must play an effect of HPAM, dissociated and activated hydrogen atoms impurities were enhanced with the hydrogen content of plasma arc increases more than 30 vol%.

3.4 Refining mechanism of HPAM

From the above mentioned results, the removal rates of impurities were enhanced with the hydrogen content of plasma arc and its dependence slightly varied with the impurity element, as indicated in eq. (5). For this refining effect of HPAM, dissociated and activated hydrogen atoms formed in the high temperature plasma arc must play an important role. Concretely, the following processes caused by hydrogen atoms are considered.

(A) Elimination of oxide thin layer and surface-active agents on the melt surface by hydrogen atoms,
(B) Enhancement of the transfer of metal vapor within the gaseous boundary layer by a dynamic interaction between hydrogen atoms and metal vapors,
(C) Increase in the surface temperature of melt, caused by high thermal conductivity of hydrogen plasma (including the recombination heat of H to H2 at the melt surface).

According to (A), the vaporization of impurities from the melted metal probably proceed more quickly due to the surface being not covered with an oxide thin layer. However, it is difficult to say that (A) is dominant in the refining effect in HPAM because the dependence of the removal rates of impurities on the hydrogen content can not be explained well by (A).

In the case of vacuum melting, it is well known that more volatile impurities than the melted metal can be easily vaporized and removed from the melted metal, although it is accurately dependent on the activity coefficient of the impurity element in the melt, according to eq. (7). On the other hand, the removal of impurities becomes difficult in a melting treatment under an inert gas at atmospheric pressure, because the vaporization rates of metals decrease by about four orders of magnitude compared with that in vacuum. This is caused by the transfer of metal vapors being considerably hindered at the gaseous boundary layer under atmospheric pressure.

However, the removal of impurities by vaporization during HPAM under atmospheric pressure, without using high vacuum, was surely observed. This result suggests a certain driving force, like the effect of (B), to enhance the vaporization of the impurities from the melted surface. In detail, it is the counter-diffusion of activated hydrogen atoms in the gaseous boundary layer, which traps the vaporized impurity metals (m_i) at the vicinity of the surface of the melted metal and transfers them through the gaseous boundary layer to the gas phase, as represented by eq. (6). In eq. (6), \( m_{ix-H_2} \) means the metal vapors trapped by hydrogen atoms, which can be supposed to be like a cluster of metal vapors and hydrogen atoms. In this process, the hydrogen atom can be taken as a carrier of the metal vapors from the melted metal surface to the gas phase and, for the some different dependence of the vaporization rate of each metallic impurity \( m_i \) on the hydrogen content observed in Fig. 6, it can be explained by the formation way of the clusters between \( m_i \) and H, as shown in eq. (6). Then the process (B) is thought to be one of the probable refining mechanism of HPAM, but further examinations, such as spectral analysis of the plasma gas-molten metal interface, will be needed to verify the progress of eq. (6) during HPAM.

\[
\begin{align*}
- \frac{d\{\text{m}_i\}}{dt} &= k_{mi}(\%H_2)^{0.5-0.9}\{\text{m}_i\} \\
\text{m}_i: &\text{ metallic impurity}
\end{align*}
\]

According to Langmuir’s equation for vacuum melting, the vaporization rate \( (dn_{mi}/dt) \) of a metallic impurity \( m_i \) from the melted metal can be expressed as eq. (7). \( n_{mi}, P_{mi}, M_{mi}, \gamma_i, N_{mi} \) and \( R \) stand for the mole number of \( m_i \), the vapor pressure of pure \( m_i \), the atomic mass of \( m_i \), the activity coefficient of \( m_i \), the mole fraction of \( m_i \) and gas constant, respectively.

\[
\frac{dn_{mi}}{dt} = \sqrt{\frac{M_{mi}}{2\pi RT}} \cdot \gamma_{mi}N_{mi}P_{mi}^\circ
\]

Since \( P_{mi}^\circ \) generally increases with the temperature \( T \), \( dn_{mi}/dt \) enhances with \( T \). This means that the evolution rate of \( m_i \) from the melted metal increases with its surface temperature. So, for the case of HPAM as well as vacuum melting, the vaporization rate of impurities will increase with the surface temperature of the melted metal. According to the process (C), the surface temperature will be raised by increasing the hydrogen content of plasma arc. Therefore, the effect of (C) may also contribute to enhance the vaporization of impurity during HPAM.

4. Conclusions

Refining and purification for two kinds of Hf metal, a high-purity Hf (HP-Hf) with 99.7 mass% and a low-purity Hf (LP-Hf) with 98 mass%, by hydrogen plasma arc melting (HPAM) has been examined and the following results have been obtained.

Almost all impurities, except for Zr and W, in the melted Hf were removed to the very low levels by vaporization during HPAM and their removal rates increased with the hydrogen content of plasma arc. Concretely, the total impurity concentrations of HP-Hf and LP-Hf, except for Zr, O, N and C, decreased from about 100 to 5 mass ppm and from about 900 to below 20 mass ppm, respectively, after 60 min of 20%H2+Ar plasma arc melting. Then, the purity of LP-Hf and HP-Hf improved to nearly 99.998% and above 99.999%, respectively. Consequently, the refining effect of...
HPAM under atmospheric pressure was proved to be superior to that of EBM under high vacuum for the removal of Fe, Al, Cu and Ti from Hf. In addition, the evaporation loss of Hf after the HPAM was considerably small to be less than 1%, notwithstanding the excellent refining result. Therefore, HPAM has been confirmed to be a very useful method for purification of Hf.

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REFERENCES