Removal of metallic impurities from zirconium by hydrogen plasma arc melting

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Zr has found a new application as a lining material of nuclear fuel element [1] and has also used prospective materials (Zr-based oxides) as high-k gate dielectrics for advanced MOS FETs [2]. It is widely regarded that the decrease of defect concentration is very important to control material properties in the field of nano-scale film technology. Since metallic impurities in the dielectric films can affect the defect formation and, consequently, to deteriorate the interface quality and reliability, the removal of the impurities plays an important role to determine the properties of gate dielectrics. Then, it is needed to utilize a high-purity source to obtain an excellent gate oxide layer with uniformity and lower defect density. Despite of requiring a high-purity source for the film deposition, to our knowledge, detailed impurity analysis and purification of Zr metal have not been carried out.

It has been found that hydrogen plasma arc melting (HPAM) enables the removal of non-metallic impurities from Fe, Mo, and Ta and also metallic impurities from Zr alloy and Nb [3–6]. For example, Mimura *et al.* [6] have revealed that Fe content in a Zr-1 mass% Fe alloy was reduced from 1 mass% to a few mass ppm level after 50 vol% H_2–Ar plasma arc melting for 180 min at a reduced pressure, while the reduction of Fe was very little when Ar plasma gas was only used. Furthermore, the impurity elimination was found to be more effective for higher H_2 content in the plasma gas. Therefore, in the present study, removal of metallic impurities from Zr by HPAM has been carried.

Experiments were carried out using a laboratory-scale plasma arc furnace equipped with a transferred arc type plasma torch, the detailed constitution of which has been described in elsewhere [6]. The specimen was set on a water-cooled copper crucible of 45 mm in diameter and 4 mm in depth. After the specimen (about 30 g) was melted down by Ar plasma arc heating, hydrogen was added to the Ar plasma gas to obtain the desired content under atmospheric pressure. The distance between the tip of the plasma torch and the melted specimen was about 20 mm. High purity argon gas (>99.9995%) and hydrogen gas (>99.9999%) were mixed and introduced into the plasma torch at a flow rate 5 l/min. The hydrogen content in the plasma gas was varied from 0 to 20% at atmospheric pressure. The specimen after first melting was melted again turning upside down for uniform refining. The GDMS (VG ELEMENTAL: VG9000) was used for precise analysis of impurity content in Zr specimens before and after plasma arc melting.

Impurity concentrations in Zr metal determined by GDMS analysis after plasma arc melting for 60 min under different plasma gases are shown in Table I. Under the atmospheric pressure, since the addition of higher H_2 content than 20 vol% to the Ar plasma resulted in an unstable arc condition, the experimental data could be obtained with H_2 concentration of 20 vol%. Approximately, the initial purity of Zr as a starting material showed above 99.946%. When Ar was only used as a plasma gas, a little or no reduction in the contents of almost metallic impurities was observed. However, the contents of Al, Cr, Mn, Fe, Ni, and Cu were found to be remarkably reduced by HPAM and their removal degree was further improved by increasing the hydrogen content in the plasma gas. The purity of Zr metal was improved up to 99.992% after 20% H_2–Ar plasma arc melting for 60 min. This result suggests that HPAM is very effective for elimination of metallic impurities from Zr metal.

In contrast to the trend of decreasing the content of above impurities, only W element considerable increased up to 20.7 mass ppm when Ar plasma arc melting was performed. This result was due to using W rod cathode in the plasma torch. W can be oxidized easily even under low oxygen pressure, and W oxides that were formed under Ar atmosphere in high temperature contaminate a base metal. This undesirable contamination from a W rod cathode, however, could be sufficiently suppressed by an addition of H_2 to the Ar plasma and a control of melting condition. This was confirmed from the present result that the content of W was remarkably reduced down to 4.85 mass ppm under the condition of 20% H_2–Ar plasma arc melting.

Fig. 1 shows the melting time dependence of main impurity concentrations in Zr metal under the deferent H_2 content in the plasma gas. In the case of Al, Cr, Fe, and Ni elements, the contents of these elements could be reduced down to just several mass ppm (1–3 ppm) after 20% H_2–Ar plasma arc melting for only 60 min, while high reduction rate could not be obtained for these elements by only Ar plasma arc melting. On the other hand, both methods of Ar plasma arc melting and the H_2 addition to the plasma lead to a good removal of Cu and Mn elements despite of small initial concentrations.

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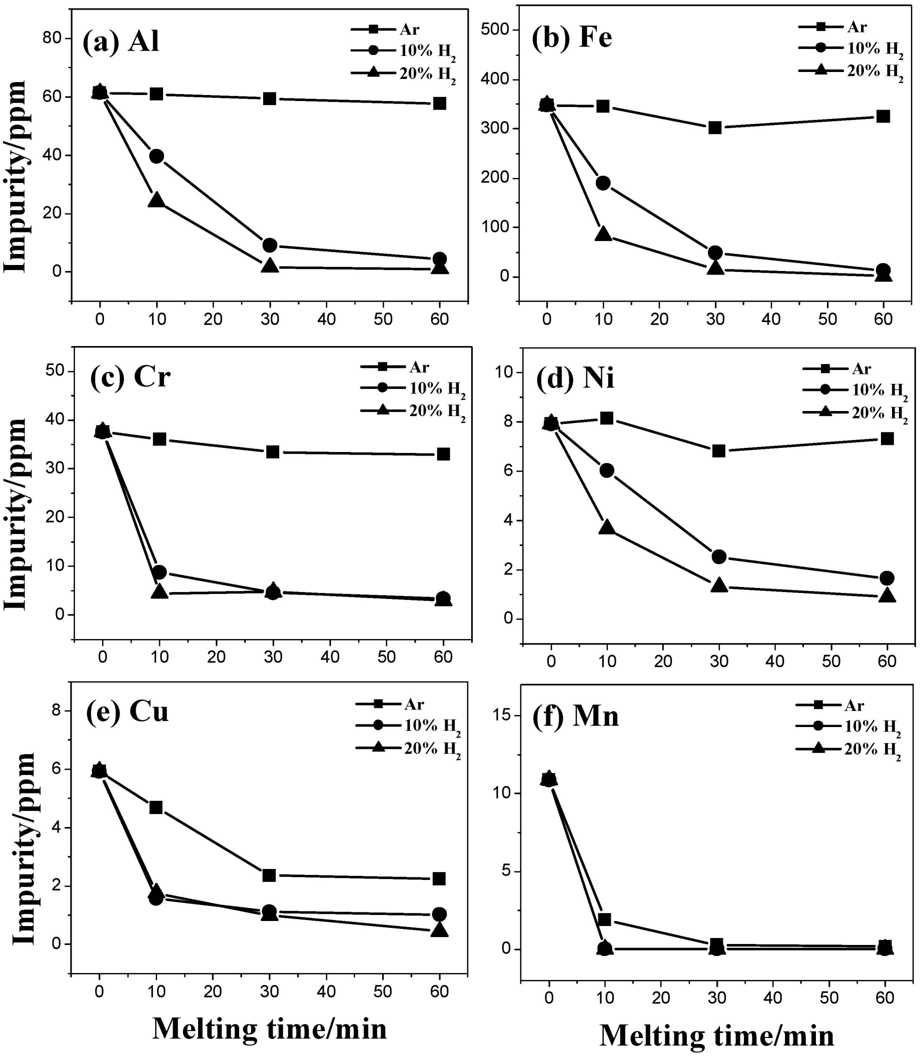

Figure 1 Melting time dependence of main impurity concentrations in Zr metal under the deferent H_2 content in the plasma gas.

The removal of elements from a base metal can be described as a sequence of the following effects: (a) elimination of the oxide layer on the molten surface by hydrogen atoms with a strong reducing power [5], (b) increase in temperature of the molten metal surface due to the higher thermal conductivity of the hydrogen plasma including the heat of recombination of 2H to H_2 [3, 7], and (c) enhancement of the transfer of metal vapor within the gaseous boundary layer by a dynamic interaction between the hydrogen atoms and the metal vapor [6].

TABLE I Impurity concentrations in Zr metal by Ar and hydrogen plasma arc melting for 60 min

Impurity	Starting material	Ar	10% H_2 +Ar	20% H_2 +Ar
B	<0.05	<0.05	<0.05	<0.05
Al	60.8	57.7	4.33	1.05
Si	5.86	5.72	1.31	2.79
P	1.69	1.67	1.61	1.31
S	1.61	2.52	1.47	1.72
Ti	16.3	16.1	16.3	16.7
Cr	37.5	34.0	3.36	3.02
Mn	10.7	0.20	0.03	0.02
Fe	342	323	12.3	1.29
Ni	7.92	7.32	1.68	0.91
Co	0.31	0.31	0.45	0.45
Cu	5.78	2.24	1.01	0.43
Zn	0.56	0.58	0.59	0.42
Mo	0.77	0.96	0.69	0.64
Hf	25.8	25.1	25.4	25.8
W	0.25	20.7	8.44	4.85
Purity (mass%) (except C, N, O)	>99.946%	>99.948%	>99.990%	>99.992%

According to the effect (a), it is supposed that vaporization of the metal can proceed more easily when the surface is no covered with an oxide layer. Therefore, an enhancement of great removal of Cr, Al, Fe, Ni, and Cu impurities which could not be removed by Ar plasma arc melting was confirmed on the basis of an elimination of the oxide layer of Zr metal during HPAM. As a main effect, the effect (b) means that a rise of the metal temperature by H_2 addition to the plasma gas accelerates the impurity removal rate and an increase of the metal surface temperature leads to higher rate of the removal process as it was reported on Sn and Cu elimination from Fe [3, 8]. Furthermore, as an additional effect, it is considered that during the counter-diffusion, hydrogen atoms trap the vaporized metal within the gaseous boundary layer and transfer it to the gas phase, which means that the activated hydrogen atoms are considered to act as a carrier medium of the metal vapor as mentioned in the effect (c).

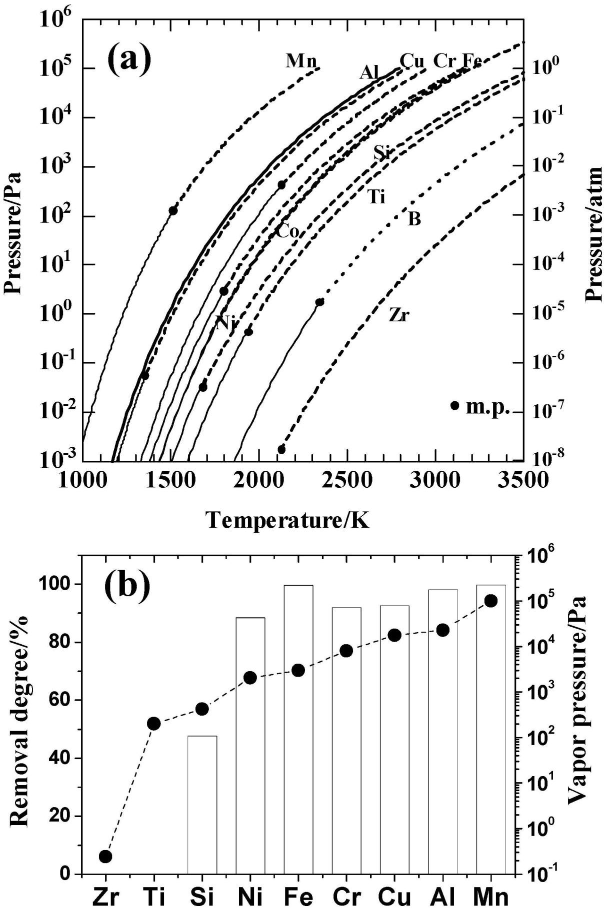

Figure 2 (a) Vapor pressures of main impurities and Zr metal as a function of temperature and (b) removal degrees of the impurities at 2500 K.

On the other hand, Mn impurity could be easily removed by only Ar plasma arc melting, which can be explained by the significant difference of vapor pressure between Mn and Zr metal. Other important mechanism is the direct vaporization in case that an impurity is present in the gas phase in contact with H_2–Ar plasma. The selective vaporization of metallic impurities is possible when a significant difference of the vapor pressure exists between the impurity and the base metal. This direct vaporization has been reported for Zn and Pb removal from Cu [9] and Sn and Cu from Fe [3]. Fig. 2a and 2b show the calculated vapor pressures of main impurities and Zr metal as a function of temperature and their relation with removal degrees of the impurities at 2500 K. All calculated vapor pressures were based on the equations from thermochemical properties of inorganic substances [10]. All elements described here have a higher vapor pressure than that of Zr metal, so that the removal of these impurities from Zr metal seems to be easily performed. As seen in Fig. 2b, the removal degree had a tendency to increase with increasing the vapor pressure of the impurities. Actually, almost impurities except for Ti and Co were removed from Zr metal. Since the initial content of Co was very small, it is difficult to clarify the behavior of the content change in this case. In the case of Ti element, it is not enough to remove sufficiently from Zr metal due to a low activity coefficient of Ti in Zr and a small difference in vapor pressure between two elements, although the vapor pressure of Ti is higher than that of Zr. Therefore, it can be simply explained the fact that low or no removal of Cr, Al, Fe, Ni, and Cu impurities by only Ar plasma arc melting and great removal degree of these impurities by H_2–Ar plasma arc melting were obtained in the present result by above-mentioned effects.

Removal of metallic impurities from commercially pure Zr metal by HPAM has been examined. It was found that HPAM has an excellent effect to eliminate impurities with higher vapor pressures than that of Zr metal. The refining effect by the addition of H_2 to Ar plasma gas lead to an enhancement of a great removal of Cr, Al, Fe, Ni, and Cu impurities which could not be removed by only Ar plasma arc melting.

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