Systematic study on helium induced nanostructure formation of 5th period transition metals for gas sensor application

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Background

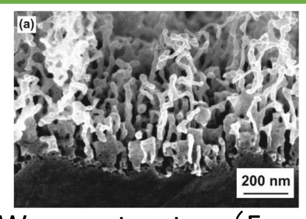


Fig.1 : W nanostructure (Fuzz)

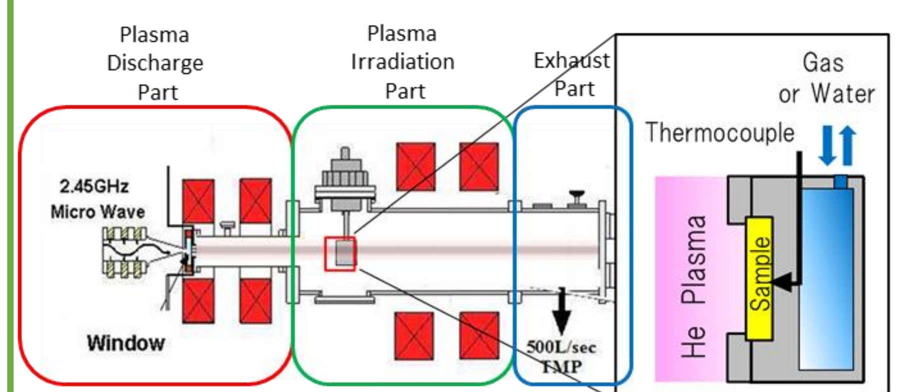
- By irradiating metal with low irradiation energy and high fluence helium (He) plasma, the surface structure of the metal changes greatly. In particular, the structure shown in Fig. 1 formed on W is called the Fuzz [1]
- In order to clarify the formation mechanism of the fibrous structure, He plasma irradiation experiments were conducted on the 6th period metal containing W under various conditions.
- Recently, the application of this nanostructure to gas sensors and ethanol sensors has been studied [2].
- A structure with a large surface area such as Fuzz is very effective for catalysts and gas sensors.
- The 5th period metals are expected to be applied to catalysts, and there are many metal elements that have been studied.

Purpose

- we conduct a He plasma irradiation experiment on the 5th period metal and W-Mo alloy in order to explore the possibility of application. In addition, it aims to acquire knowledge related to structure formation by comparing with the 6th period metal.

Experiment

【Device】
ECR plasma device



【Conditions】
- Plasma parameter
  Flux : : ~ $1.0\text{-}3.0 \times 10^{21}$ $m^{-2}s^{-1}$
  Fluence : : ~ $1.8\text{-}5.4 \times 10^{25}$ m^{-2}
  Te : ~8 eV
  ne : ~7×10^{16} m^{-3}
- Gas : He (50mTorr)
- Irradiation temperature : 300～1078K
- Incident Energy : 60~120eV

【observation】
FE-SEM

【Element analysis】
EDS

Conclusion

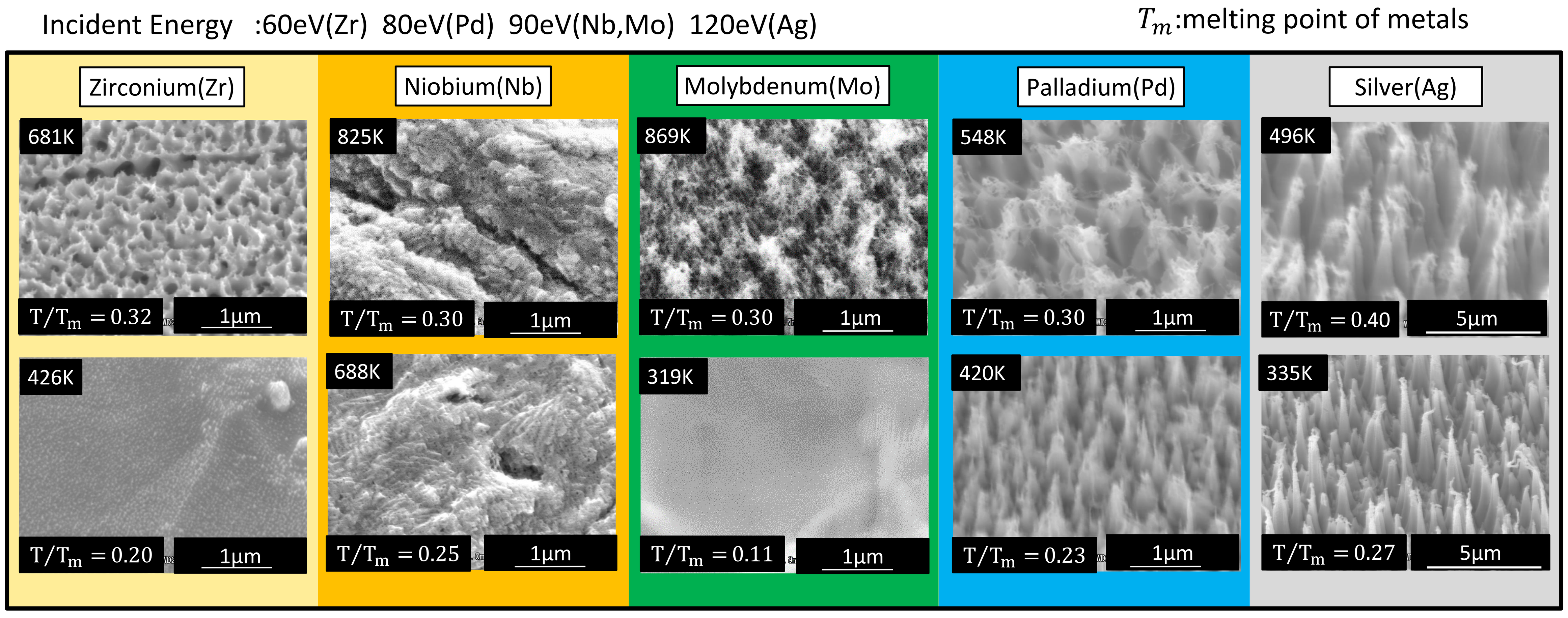
- In many 5th period metals, a fluffy fibrous structure could be confirmed. Among them, Mo is particularly easy to form a fibrous structure and is considered effective for applications such as gas sensors.
- From the comparison of the 5th and 6th period metals, it was found that very similar structures were formed especially for the 5th and 6th groups. This indicated the possibility of a group relationship.
- With regard to Zr, Pd, and Ag metals, a characteristic structure in which the fibrous structure extends from the cone-shaped tip was confirmed under specific temperature conditions.
- In W-Mo alloys, the fibrous structure of W could be formed at a lower temperature than pure W.

Result and Discussion

SEM Result

【He plasma →5th period metal】

Irradiation flux : $1.0\text{-}3.0 \times 10^{21}$ $m^{-2}s^{-1}$ Irradiation fluence : $2.0\text{-}3.0 \times 10^{21}$ $m^{-2}s^{-1}$
Incident Energy : 60eV(Zr) 80eV(Pd) 90eV(Nb,Mo) 120eV(Ag)
T:surface temperature of sample
T_m:melting point of metals



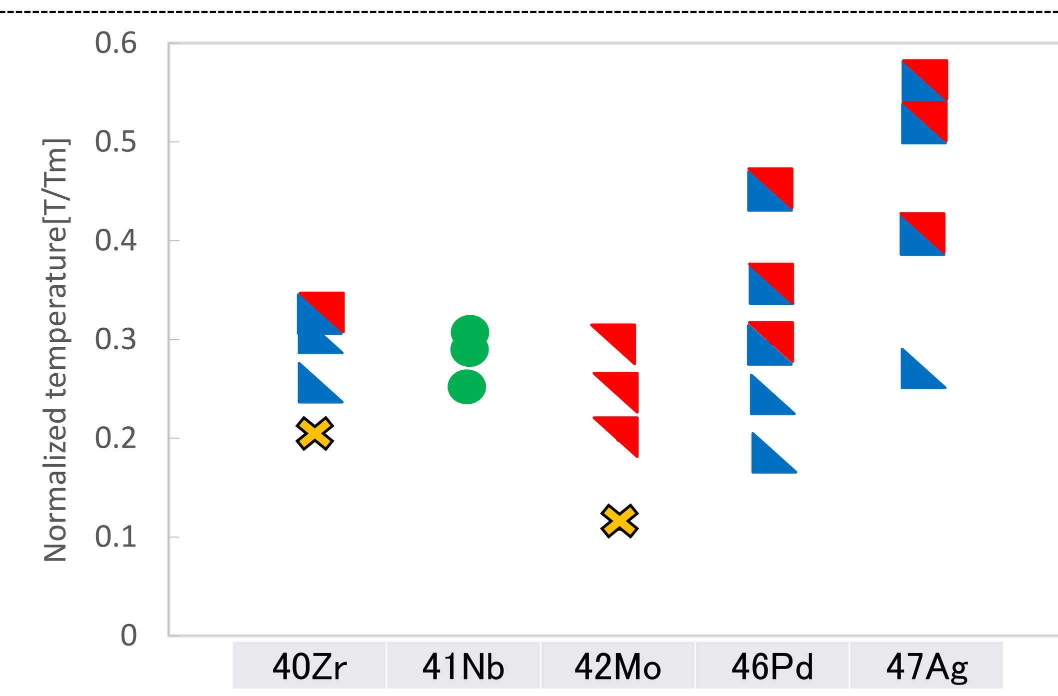


Fig.2 Normalized table for the 5th period metal

✖	No change
◣	Cone-shaped structure
◥	Fiber structure
●	Hole or other structure

- From SEM images, a fibrous structure such as fluff could be confirmed in many 5th period metals. This shows the same tendency with the 6th period metal.
- As with the 6th period metal, it was confirmed that the fibrous structure started to form from the region where the normalization temperature was 0.2 to 0.3 for many metals. Since vacancies are formed in a region where the normalization temperature is 0.2 to 0.3 in metal, it can be expected that the vacancies are related to the formation of the fibrous structure[3].
- Zr, Pd, and Ag formed a structure as shown in Fig. 3 in which a fibrous structure grew from the tip of the cone-shaped structure.
- In Nb, holes were mainly formed on the surface. This is the 6th period metal, and the same tendency is shown in Ta which is the same group as Nb.
- Mo is more likely to form a fibrous structure than other 5th period metals, and is considered effective for gas sensor applications.


Fig. 3 Schematic of the structure formed on the surface of Zr, Pd and Ag

【He plasma → W-Mo alloy】

- Group 6 metals Mo and W form very fine fibrous structures [1]
- Experiments were carried out on the assumption that a fibrous structure could be formed more easily by irradiating an alloy made using these two metals with He plasma.

【Element analysis】

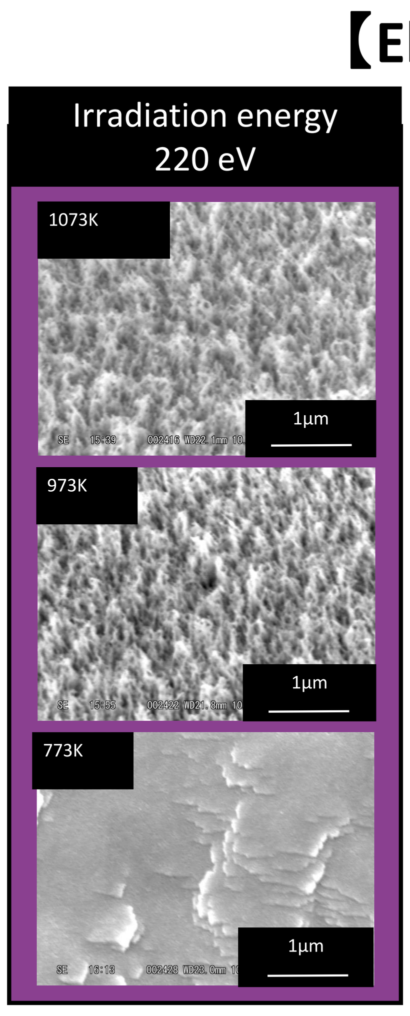


Fig.5 SEM image of temperature dependence of the surface structure of W-Mo alloy

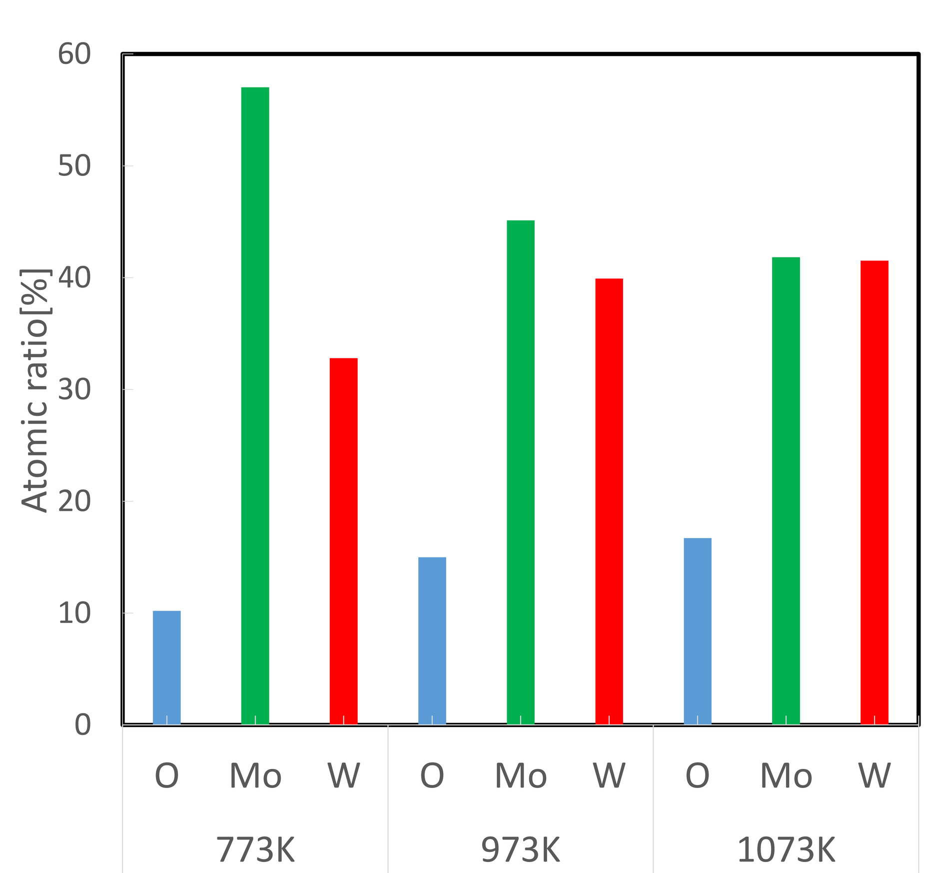


Fig.6 : Surface temperature dependence of the abundance of each element of W-Mo alloy

【Comparison between pure material and W-Mo alloy】

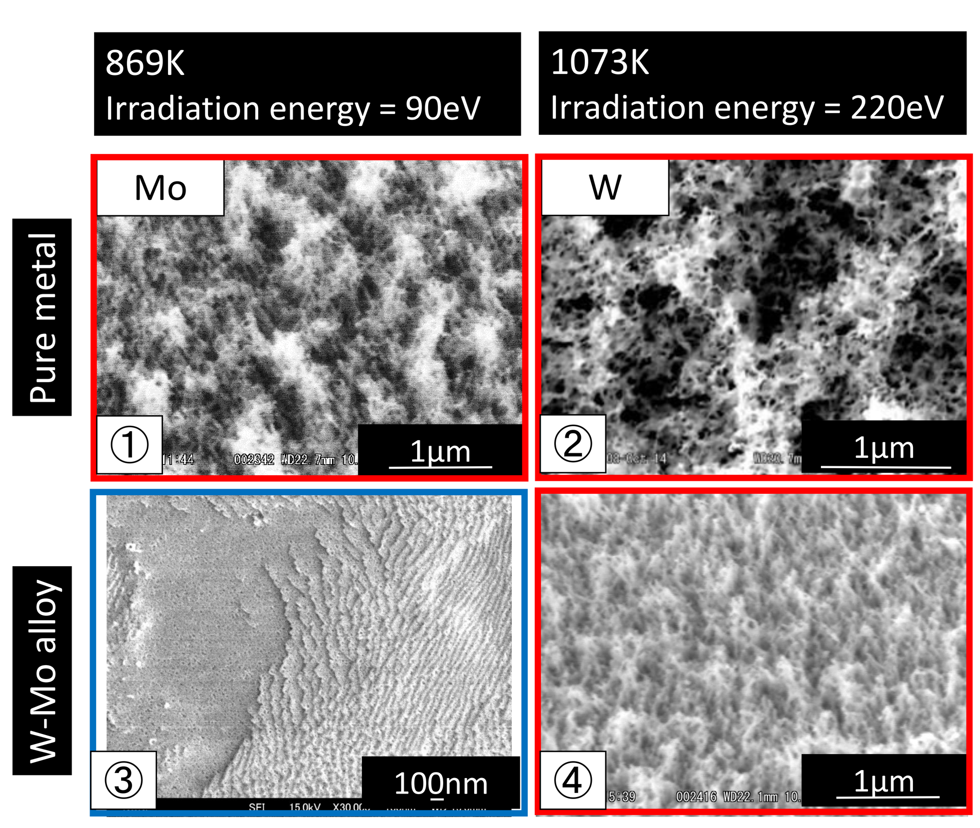


Figure 4: SEM images of pure materials and W-Mo alloys under the fibrous structure formation conditions of W and Mo.

Irradiation flux : $1.0\text{-}3.0 \times 10^{21}$ $m^{-2}s^{-1}$
Irradiation fluence : $2.0\text{-}3.0 \times 10^{21}$ $m^{-2}s^{-1}$

W-Mo alloy sample
Mass ration W : Mo = 1 : 1
Atomic ratio W : Mo = 65.8 : 34.2

- From comparison of ① and ③ in Figure 4, it was found that the presence of W hinders the formation of Mo fibrous structure.
- From the SEM image in ③ of Fig. 4, the hole and the wave-like surface structure were confirmed.

- Fig. 5 shows that the W-Mo alloy forms the fibrous structure at a temperature lower than the temperature at which pure W forms the fibrous structure due to the presence of Mo. This may be due to the fact that lattice constant of W-Mo alloy is smaller than that of pure W, and the compressive stress due to condensed He bubbles is increased.
- From Fig. 6, the percentage of Mo atoms decreased as the surface temperature increased.
- Fig.5 and 6 show that W is important for the formation of a fibrous structure in the W-Mo alloy.

Reference [1] Kajita S., Sakaguchi W., Ohno N., Yoshida N. & Saeki, Nucl. Fusion 49, 095005-6(2009)
[2] Kenzo Ibano, Yoshihiro Kimura, Tohru Sugahara, Heun Tae Lee and Yoshio Ueda Published 22 March 2018
[3] B.N. Singh a,*, J.H. Evans b, Journal of Nuclear Materials 226 (1995) 277-285