Effects of thermal treatment on structural and electrical properties of sputtered Ir-W alloy thin films

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Thermally and chemically stable electrode films are required for capacitor electrodes of semiconductor memories, such as dynamic random access memories (DRAMs) and ferroelectric random access memories (FeRAMs). In this study, iridium-tungsten (Ir-W) alloy thin films were prepared on SiO_2/Si substrates by RF magnetron sputtering, and the effects of thermal treatment in oxygen atmosphere on the structural and electrical properties of the films were studied. The surface of the as-deposited Ir-W films was very smooth and the films showed low electrical resistivities below 120 μΩcm. The resistances and the smooth surface morphology of the Ir-W (approximately 20 at.%) films remained after thermal treatment up to 600°C in oxygen, which indicates the high thermal stability of the Ir-W alloy thin films.

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1. Introduction

Recently, high-dielectric-constant and ferroelectric oxide thin films including $SrTiO_3$, $(Ba,Sr)TiO_3$, $Pb(Zr,Ti)O_3$ and $SrBi_2Ta_2O_9$ have been used as capacitors for semiconductor memories, such as dynamic random access memories (DRAMs) and ferroelectric random access memories (FeRAMs) [1]. Since these oxide thin films are deposited at high substrate temperatures in oxygen atmosphere, it is very important to examine new electrode materials that can tolerate these deposition conditions without the deterioration of surface morphology and electrical conductivity. Thin films of platinum group metals and their oxides, such as Ir, Ru, Pt, IrO_2, and RuO_2 [2-5], have attracted considerable attention as candidate capacitor electrode materials for DRAMs and FeRAMs because of their low resistivity and high chemical stability. Platinum-group-metal-based alloys, such as Ru-Ti and Ta-Ir [6,7], and their complex oxides such as Ir-Ta-O [8] have also been studied to improve the thermal stability of electrodes. In addition, thin-film materials with a high thermal stability and a high oxidation resistance are increasingly becoming important for applications as protective and hard coatings.

The thermal stability, mechanical strength and crystallization properties of some platinum-group-metal-based alloys have been studied [9-12]; however, reports on the electrical properties of these alloys are scarce. We expect superior chemical and thermal stabilities for Ir-refractory metal alloys, since Ir has a high melting temperature and a high chemical stability. Furthermore, improvement of the adhesion between electrode films and SiO_2 layers is also expected from the alloying. Previously, the thermal stability of Ir-Ta alloy thin films was studied, and good electrical and morphological properties of the films were obtained [13]. In this paper, we

report on the structural, electrical and mechanical properties and thermal stability of Ir-W alloy thin films because W has a higher melting temperature and a lower electrical resistivity than Ta.

2. Experimental

Ir-W alloy thin films with thicknesses of approximately 200 nm and 1 μm were deposited on SiO_2(100 nm) /Si substrates using an RF magnetron sputtering system. The sputtering targets were 2-inch disks of Ir (99.9% purity) and W (99.9% purity) metals. The composition of the alloy films was varied by changing the number of W (99.9% purity) chips with dimensions of 5 mm × 5 mm × 1 mm, which were placed on the Ir target. The RF power and substrate temperature during deposition were kept constant at 50 W and 500°C, respectively. The Ir-W alloy thin films were postdeposition-annealed in an electric furnace between 300°C and 800°C for 1 hour in oxygen (1 atm).

Crystal structure was evaluated by X-ray diffraction (XRD) with Cu Kα radiation and the electrical resistivity was measured by a four-point probe method. The surface morphology of the films was observed using scanning electron microscopy (SEM). The mechanical property of the films was characterized in terms of Vickers hardness under a load of 25 gf applied for 15 seconds. The chemical composition of the films was evaluated by energy-dispersive X-ray analysis (EDX). Thick samples (1 μm thick) were used for hardness and EDX measurements to reduce the influences of substrate on the measurements.

3. Results and discussion

3.1. Crystal structure, and electrical and mechanical properties of as-deposited Ir-W alloy thin films

The XRD patterns of the samples with different W concentrations are shown in Fig. 1. The crystal structure of the Ir-W alloy films changed from fcc-Ir to orthorhombic-IrW and bcc-W with increasing W content. The intensities of the diffraction peaks of the alloy films with W contents of 15 at.% and 23 at.% are very weak, and the crystal grain size estimated from the half-width of the diffraction peaks using Scherrer's equation was 10–15 nm for the alloy films. From these results, it is confirmed that fine-grained alloy films are formed at W contents of approximately 20 at.%.

Figure 2 shows the relationship between electrical resistivity and film composition. Resistivity increases with increasing W content, and a maximum resistivity of 120 μΩcm is obtained at W contents of 30–50 at.%. The increase in resistivity is thought to be caused by the decrease in crystal size and compound formation. Although the resistivities of the Ir-W alloy films are larger than that of pure Ir, the maximum resistivity is much lower than that of Ir-Ta alloy films (220 μΩcm) [13]. The resistivities of Ir–W alloy thin films are expected to be acceptable for fabricating capacitor electrodes of FeRAMs. Figure 3 shows the relationship between Vickers hardness and the composition of Ir-W films. The hardness of the Ir-W alloy films, 900–1000 Hv, is higher than those of pure Ir and W films. However, quantitative discussion on the hardness seems to be difficult because the penetration depth of an indenter was close to the film thickness (1 μm) and

the influence of substrate is supposed to be unavoidable. The increase in hardness is supposed to be caused by the decrease in crystal grain size and compound formation. Chemical bonds that confer a high mechanical hardness seem to be useful in preventing the diffusion of atoms through an electrode layer, which is important for FeRAM applications.

3.2. Effects of postdeposition annealing in oxygen

The XRD patterns of the Ir-W (15 at.%) film before and after annealing in O_2 ambient are shown in Fig. 4. After oxygen annealing at temperatures up to 600°C, no marked change in the XRD patterns was observed. However, the diffraction peaks corresponding to IrO_2 and WO_3 are clearly observed after annealing at 700°C. In addition, metal fcc-Ir peaks are clearly observed even after annealing at 800°C, indicating that the oxidation of the film is restricted to only a small part of the film. Furthermore, the intensity and width of the Ir peaks respectively increases and decreases with increasing annealing temperature, which indicates that the crystallinity of the Ir-W film is improved by the heat treatment. From these results, the Ir-W (15 at.%) film is thought to be stable up to 600°C in O_2 ambient, although part of the film begins to be oxidized at 700°C. The diffraction peaks due to IrO_2 were also observed for the pure Ir film after annealing at 700°C. Figure 5 shows the surface SEM images of the Ir-W (15 at.%) film before and after annealing at 500–800°C. The surface of the film remains flat after thermal treatment up to 600°C, and no structural defects, such as hillock formation and film peeling, are observed. However, the surface of the film becomes slightly rough at 700°C, and particles with a diameter of approximately 1 μm are formed on the film surface at 800°C. The particles are presumed to be WO_3 crystals since a much higher W content was

obtained for the area of the particles than for the flat film surface, according to the result of EDX analysis.

The sheet resistances of the Ir-W alloy films with various W contents are plotted as functions of annealing temperature in Fig. 6. No remarkable change in resistance is observed for the pure Ir film, and a slight decrease in resistance is found for the Ir-W (15 at.%) film above 600°C. Although oxide formation was observed for the Ir-W (15 at.%) film at 700°C as shown in Fig. 4, no adverse influence of oxidation on resistance was observed. It is presumed that W atoms migrate preferentially to the film surface and form an oxide layer; as a result, the W content of the Ir-W alloy film decreases. Therefore, the resistivity of the Ir-W film is thought to decrease due to the decrease in the amount of W, which acts as a scattering center of electrons, in the alloy film. Due to their low resistance and flat surface morphology after annealing in oxygen, the Ir-W alloy films are thought to be applicable as capacitor electrodes of DRAMs and FeRAMs. In contrast, the resistances of the pure W film and Ir-W alloy (54 at.%) film increase abruptly at annealing temperatures of 400°C and 500°C, respectively, due to oxidation and the formation of insulating or semiconducting WO_3. Figure 7 shows the sheet resistances of the Ir-W films before and after annealing at 500 °C, which is the typical deposition temperature of ferroelectric $Pb(Zr,Ti)O_3$ films, as functions of film composition. No marked difference between the resistances before and after annealing is observed for the Ir-W alloy films with W contents below 30 at.%; however, the resistances of the films with higher W contents increase markedly after annealing due to oxidation.

4. Conclusions

Ir-W alloy thin films with electrical resistivities below 120 μΩcm were prepared by sputtering. The surface of the Ir-W alloy films was found to be very flat. After heat treatment up to 600°C, no marked oxidation was observed for the Ir-W alloy films with W contents of approximately 20 at.%, and the films maintained their low resistance and flat surface morphology. From these results, Ir-W alloy is concluded to be a suitable DRAM and FeRAM capacitor electrode material.

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Figure captions

Fig. 1. XRD patterns of Ir-W alloy thin films with various W contents.

Fig. 2. Electrical resistivity of Ir-W films as a function of film composition.

Fig. 3. Vickers hardness of Ir-W films as a function of film composition.

Fig. 4. XRD patterns of Ir-W (15 at.%) films before and after annealing in oxygen atmosphere.

Fig. 5. Surface SEM images of Ir-W (15 at.%) alloy films before and after annealing in oxygen.

Fig. 6. Sheet resistances of Ir-W alloy thin films as functions of annealing temperature.

Fig. 7. Sheet resistances of Ir-W alloy thin films before and after annealing in oxygen at 500°C for 1 hour as functions of composition.

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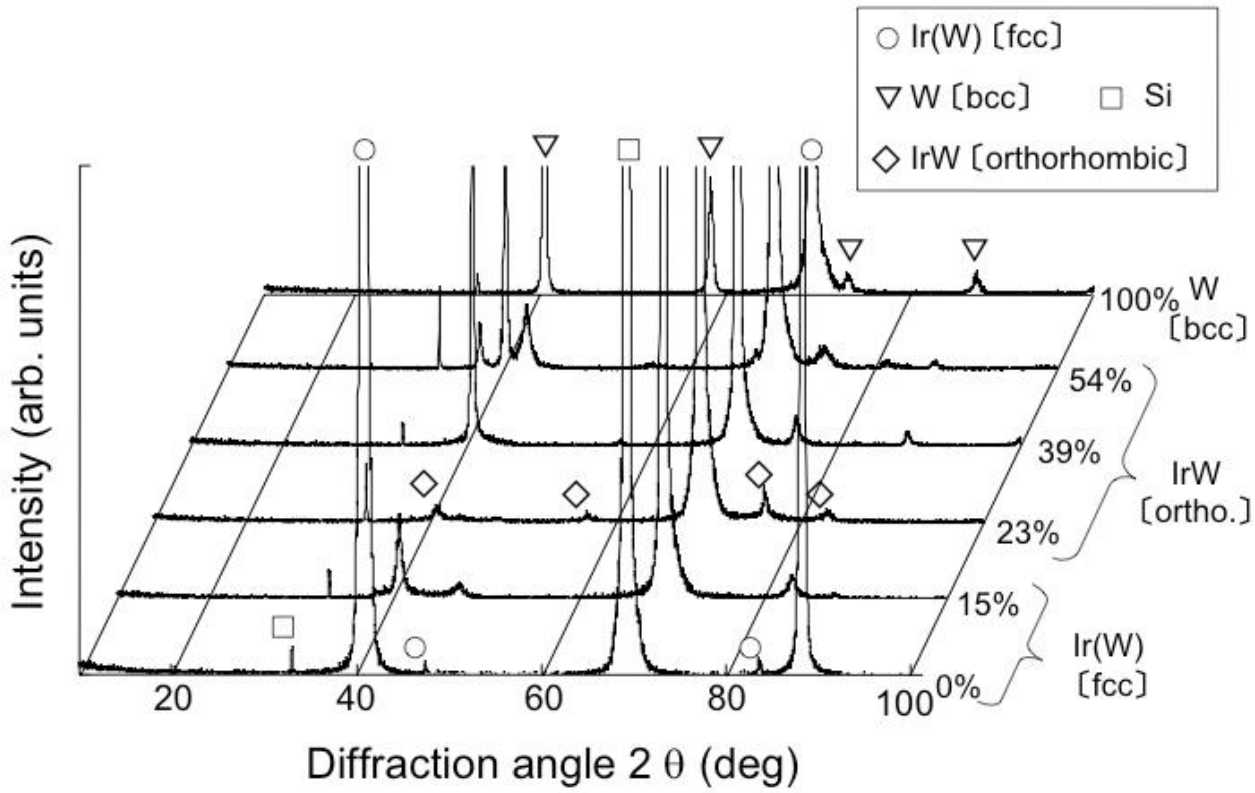
○ Ir(W) [fcc]
▽ W [bcc]
□ Si
◇ IrW [orthorhombic]
Intensity (arb. units)
100% W [bcc]
54%
39%
23%
IrW [ortho.]
15%
0%
Ir(W) [fcc]
20
40
60
80
100
Diffraction angle 2 θ (deg)

Fig. 1

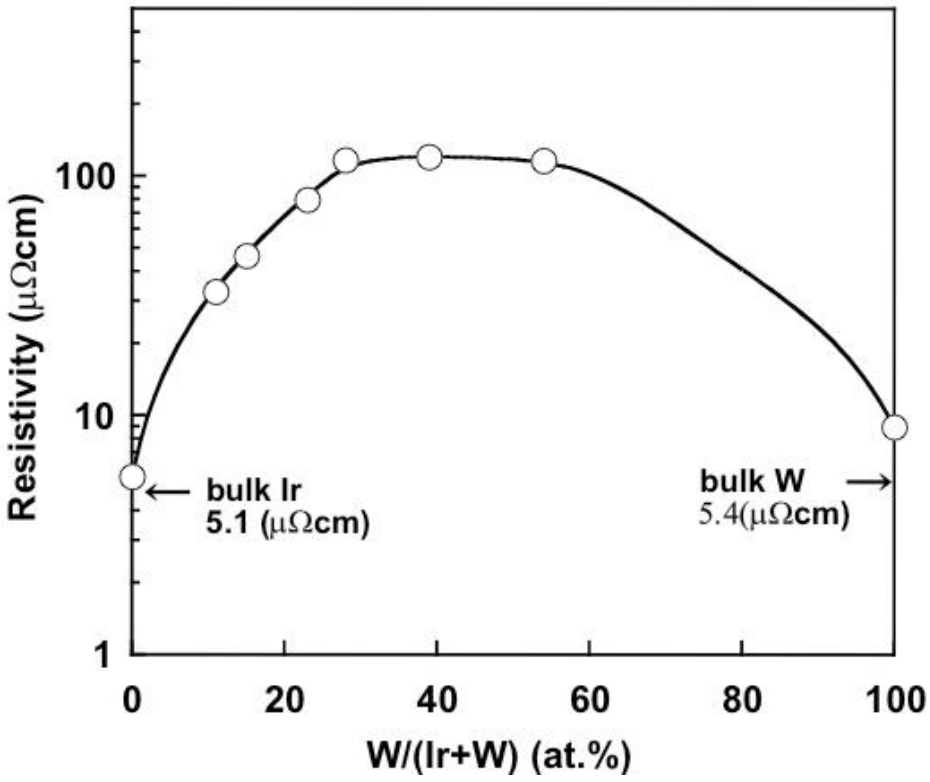
Resistivity (μΩcm)
100
10
1
0
20
40
60
80
100
W/(Ir+W) (at.%)
bulk Ir
5.1 (μΩcm)
bulk W
5.4(μΩcm)

Fig. 2

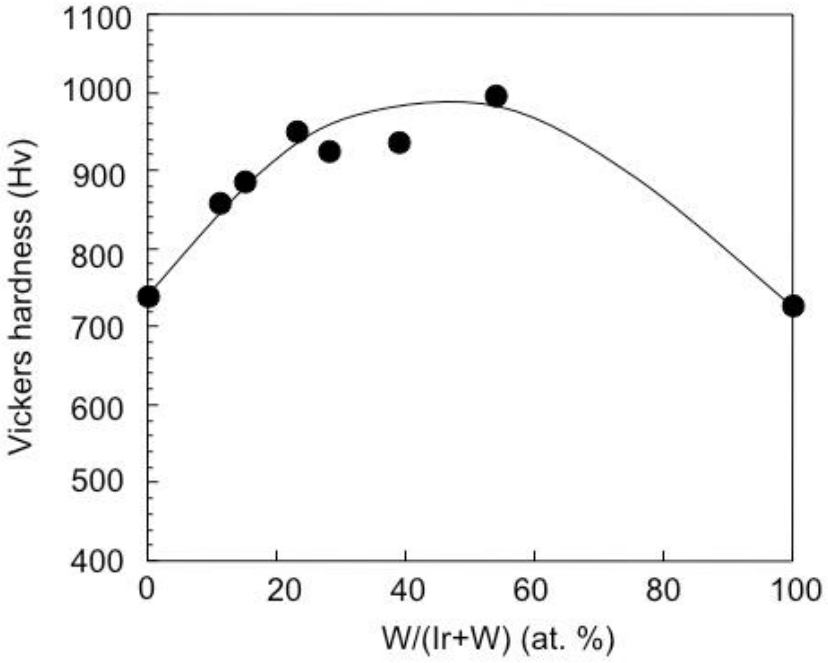
Vickers hardness (Hv)
1100
1000
900
800
700
600
500
400
0
20
40
60
80
100
W/(Ir+W) (at. %)

Fig. 3

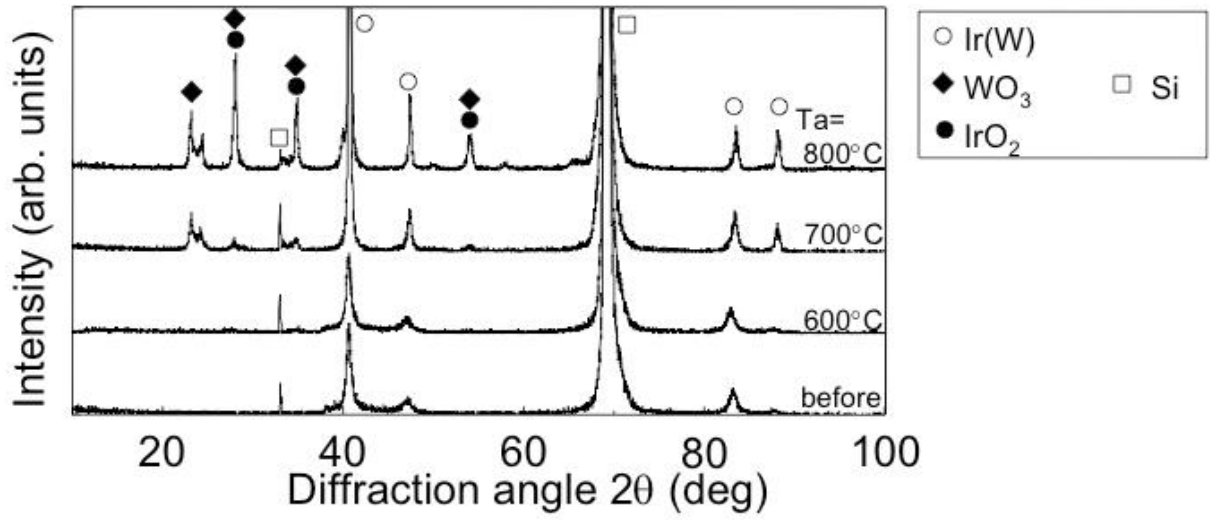
Intensity (arb. units)
Diffraction angle 2θ (deg)
20
40
60
80
100
Ta=
800°C
700°C
600°C
before
Ir(W)
WO3
IrO2
Si

Fig. 4

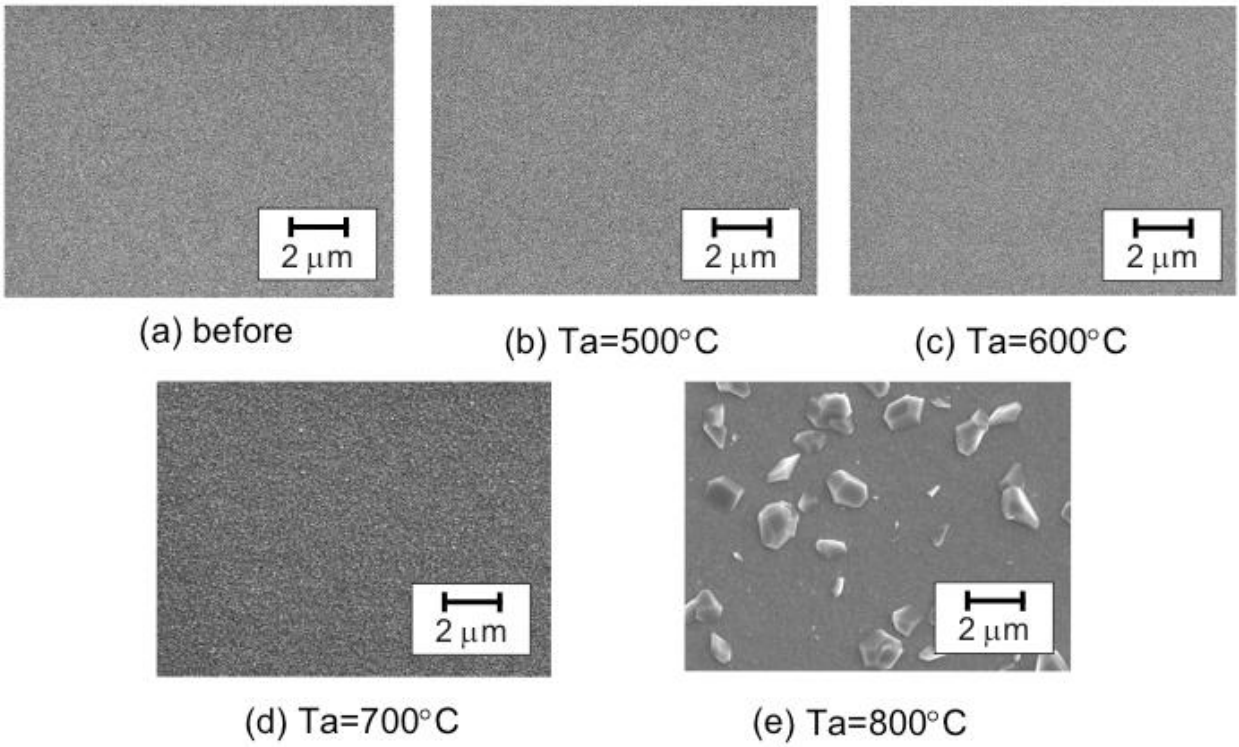
2 μm
2 μm
2 μm
(a) before
(b) Ta=500°C
(c) Ta=600°C
2 μm
2 μm
(d) Ta=700°C
(e) Ta=800°C

Fig. 5

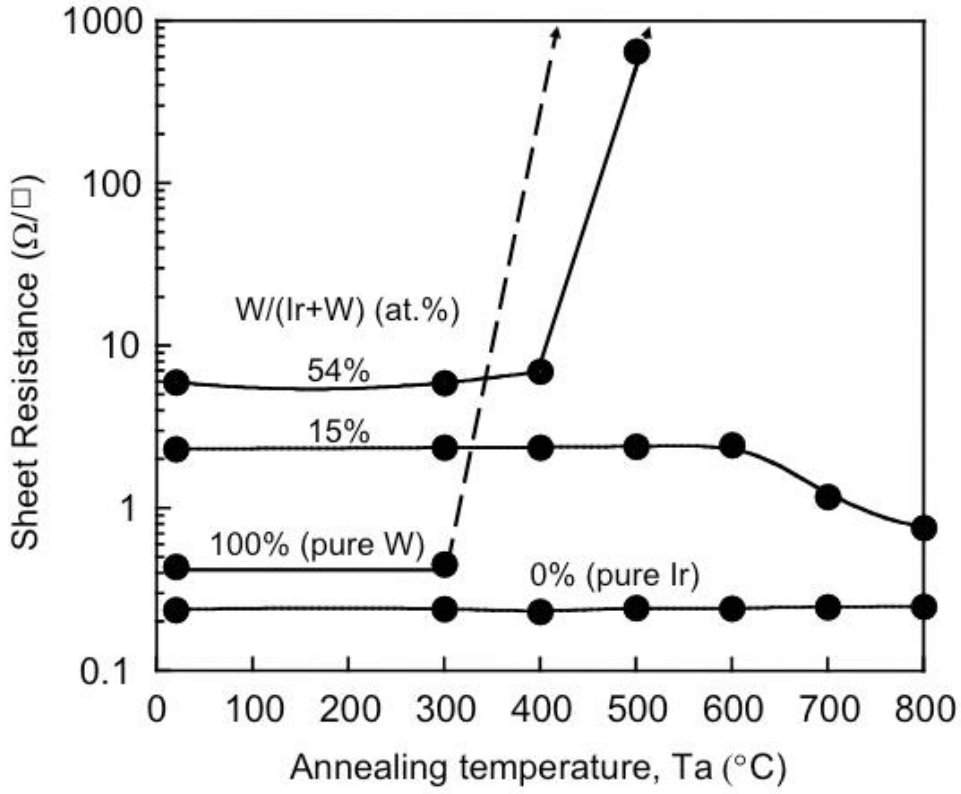
1000
100
10
1
0.1
Sheet Resistance (Ω/□)
W/(Ir+W) (at.%)
54%
15%
100% (pure W)
0% (pure Ir)
0
100
200
300
400
500
600
700
800
Annealing temperature, Ta (°C)

Fig. 6

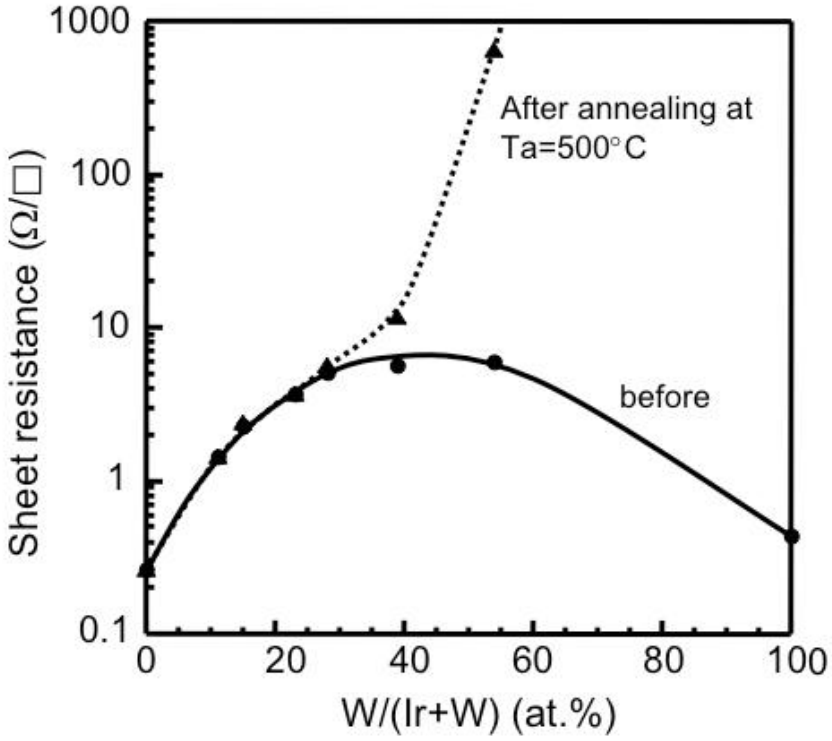
1000
100
10
1
0.1
Sheet resistance (Ω/□)
0
20
40
60
80
100
W/(Ir+W) (at.%)
After annealing at
Ta=500°C
before

Fig. 7