

# Proposal of Porous Chromium Film Fabrication Method for an IR Absorber

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## ABSTRACT

Novel fabrication method of porous Chromium (Cr) film for an infrared (IR) absorber is proposed and total absorption factor above 96.2% at about 10  $\mu\text{m}$  of IR wavelength, which is corresponding to the peak wavelength of our body temperature of 37  $^{\circ}\text{C}$ , is achieved. The porous Cr film is formed on the silicon substrate. Our infrared absorber is composed of porous Cr film remained after chemical etching removal of co-sputtered copper (Cu) with Cr, and the composition rate of Cu and Cr is varied so as to be the graded composition film: Cr:Cu (20:80)/ Cr:Cu (50:50) / Ti (as an underlying metal) on the thermally grown  $\text{SiO}_2$  thin film formed on the Si substrate.

**Keywords:** IR absorber, porous Chromium, Silicon, graded material, needle-like crystals

## 1 INTRODUCTION

Many kind of IR absorbers have been used for thermal IR sensors, such as gold black, infrared absorbing dyes, and silicon nitride film, however, they have problems for micromachining fabrication process using the alkaline anisotropy etchant, such as hydrazine [1], [2]. The stable and high absorption film in infrared wavelength of 8-14  $\mu\text{m}$  are strongly demanded, especially for the human body temperature detection.

## 2 CONCEPT OF THE IR ABSORBER AND FABRICATION METHOD OF THE POROUS CHROMIUM FILM

In this paper following essential matters for the infrared absorber (IR absorber) are considered. 1. The infrared absorber should have many free electrons in it, because their motions due to their acceleration by the induced electric field originated from the incident infrared light make energy loss by collisions at grain (particle) boundaries. This fact leads to that the infrared absorber should be composed of high conductivity materials such as metals and be less rusty metals (only surface oxidation is allowed). 2. Most of free electrons in the metal particle should lose the kinetic energy within one period of the infrared light. This fact leads to the suitable particle size of the infrared absorber. 3. Reflection from the infrared absorber should be less. This fact leads to that the surface

region of the infrared absorber should be less density. 4. The effective optical thickness of the infrared absorber will be better to be about 1/4 of peak wavelength (10  $\mu\text{m}$ ) at 37  $^{\circ}\text{C}$  because of interference effects between the incident IR and the reflected one.

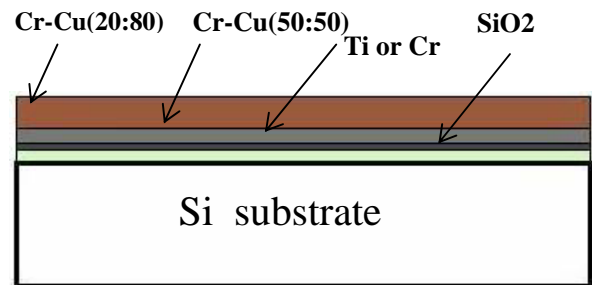


Fig.1 Multilayer of Cr-Cu with different composition deposited on the Si substrate.

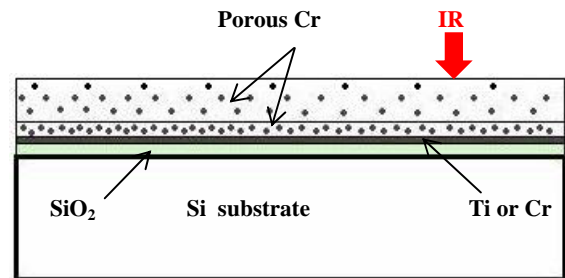


Fig.2 Porous Cr film after etching removal of Cu component shown in Fig.1 as an IR absorber.

Our infrared absorber is composed of porous Cr film remained after chemical etching removal of co-sputtered copper (Cu) with Cr, and the composition rate of Cu and Cr is varied (graded composition film: Cr:Cu (20:80)/ Cr:Cu (50:50) / Ti or Cr (as an underlying metal)) according to the essential matters described above. In Fig. 1 multilayer of Cr-Cu with different composition formed on the Si substrate is shown. In Fig. 2 a sketch of the porous Cr film after etching removal of Cu shown in Fig.1 as an IR absorber is shown.

## 3 EXPERIMENTAL RESULTS

### 3.1 Morphology Dependences of Crystallized Cr on the Underlying Metals and the Substrate Temperature $T_s$

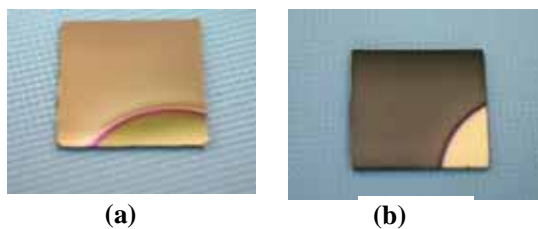


Fig.3 Sputtering deposited Cr-Cu film on the Si substrate shown in Fig.1 (a), and porous Cr film shown in Fig.2 (b) for Ti as the underlying metal.

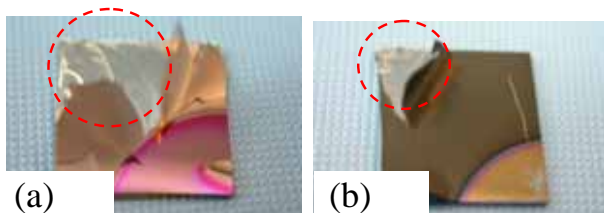


Fig. 4 Sputtering deposited Cr-Cu film come off and clacked inside the Si substrate before Cu etching removal (a) and after that (b) for the Cr underlying metal at 300 °C.

Sputtering deposited Cr-Cu film (Cr:Cu (20:80)/ Cr:Cu (50:50) / Ti on the SiO<sub>2</sub> thermally formed on the Si substrate ) at the substrate temperature Ts of 400 °C before Cu etching removal as shown in Fig.1 (a) and the porous Cr film after the chemical etching of Cu component using the nitric acid as shown in Fig.2 (b) are shown in Fig.3 (a) and (b), respectively. Conditions of the sputtering depositions as a series experiments are as follows: Ti: 3min.(200W); Cr-Cu (50:50):8min. (500W); Cr-Cu (20:80): 1hr .(500W).

We can see that there are no clacks on the deposited Cr-

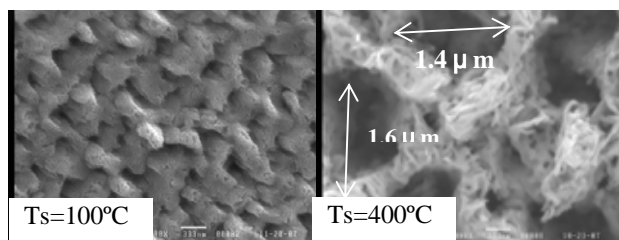


Fig. 5 SEM images of sputtering deposited Cr-Cu films after Cu etching removal for different Ts for the Ti underlying metal.

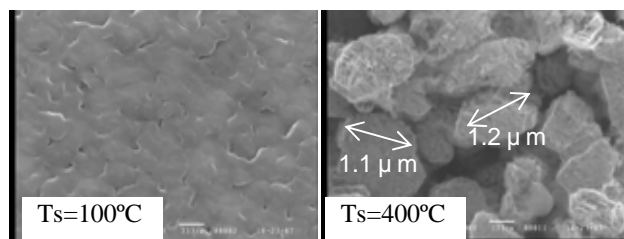


Fig. 6 SEM images of sputtering deposited Cr-Cu (20:80) films after Cu etching removal for different Ts for the Cr underlying metal.

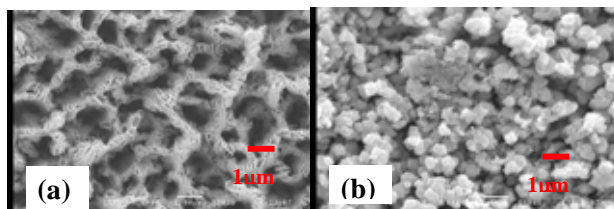


Fig. 7 SEM images of Cr-Cu (20:80) (a), and Cr-Cu (50:50) (b) deposited at Ts=400 °C after Cu etching removal.

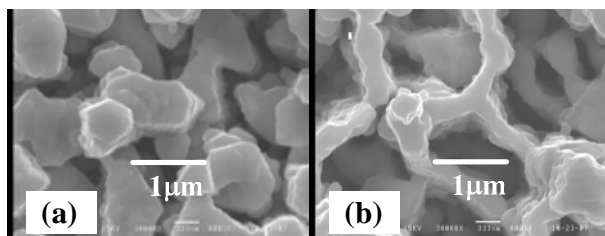


Fig. 8 SEM images of Cr-Cu (20:80) deposited at Ts=400 °C before Cu etching out for different underlying metals of Cr (a) and Ti (b)

Cu film for this Ti underlying metal, however, most deposited Cr-Cu films formed above Ts>200°C for the underlying metal of Cr film are come off and cleaved inside the silicon substrate but not at the boundary of the deposited Cr-Cu film and the SiO<sub>2</sub> film as shown in Fig.4 (a) and (b). The thermally grown SiO<sub>2</sub> film layer of about 0.3 μm thick on the Si substrate is lost in this case of Cr underlying metal.

In Fig.5 SEM images of porous Cr film deposited at different substrate temperature Ts of 100 °C and 400 °C and deposited on the Ti film as the underlying metal, and in Fig.6 that on the Cr film are shown.

We have found that morphology of crystallized Cr in the co-sputtered Cu depends strongly on the underlying metal of Cr and Ti, and also on the substrate temperature Ts, and that as to the Cr film, mesh-like crystals composed of

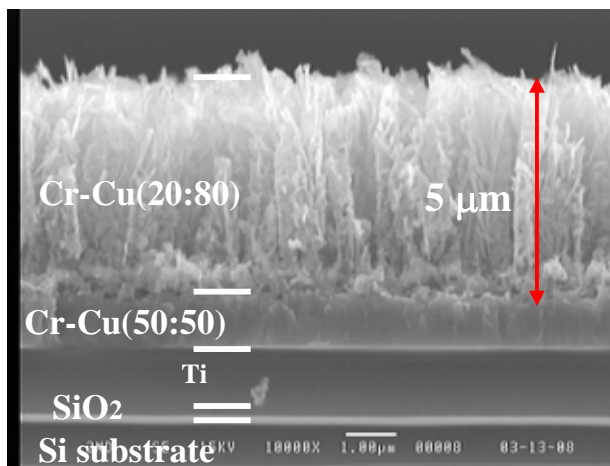


Fig. 9 Cross sectional view of the porous Cr film deposited on the Ti film at Ts=400°C.

many needle-like crystals are grown.

In Fig.7 comparison of SEM images of Cr-Cu (20:80) (a), and Cr-Cu (50:50) (b) deposited at  $T_s=400^\circ\text{C}$  after Cu etching removal are shown. From these Fig.7 (a),(b) we can see that larger Cu content in the sputtering deposited films from different Cu : Cr ratio targets leads to the mesh structured film.

In Fig.8 SEM images of Cr-Cu (20:80) deposited at  $T_s=400^\circ\text{C}$  before Cu etching removal for different underlying metals of Cr (a) and Ti (b) are shown. We can see that porous Cr-Cu (20:80) films composed of many layers are grown at this time before the Cu etching removal. We have confirmed that these porous Cr-Cu (20:80) film composed of many layers are already formed at the temperature below  $T_s=100^\circ\text{C}$  although their pore sizes become less than that formed at higher  $T_s$ . We can find that the porous Cr-Cu (20:80) composed of rich Cu film material as shown in Fig.8 has needle-like Cr crystals inside these porous but planar materials judging from the appearance of needle-like Cr crystals after Cu etching removal as shown in Fig. 5 ( $T_s=400^\circ\text{C}$ ) and Fig. 7 (a).

In Fig.9 cross sectional view of the porous Cr film deposited on the Ti film as the underlying metal at  $T_s=400^\circ\text{C}$  is shown. We can see that the porous Cr film is composed of the perpendicular nano size needle-like crystals.

### 3.2 IR Spectra for Transmissivity T and Reflectivity R of the Porous Cr

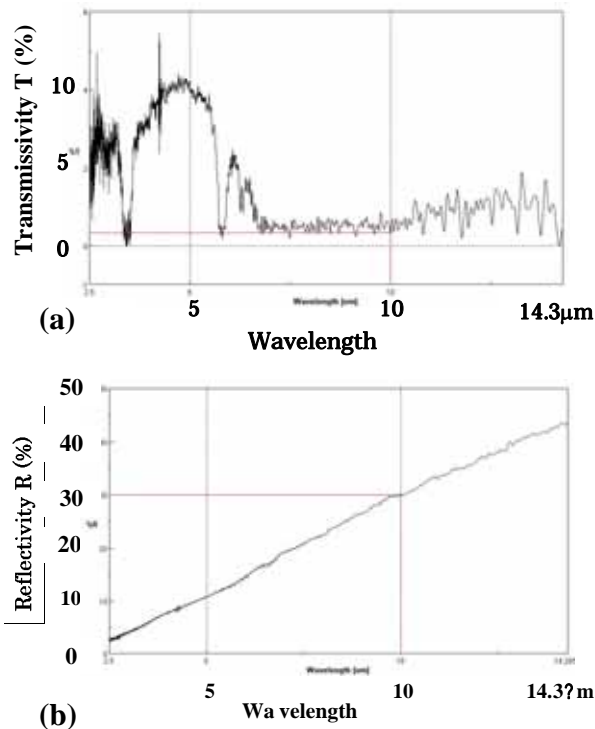


Fig.10 Spectra of the transmissivity T (a) and the reflectivity R (b) of the porous Cr film as an IR absorber at  $T_s=100^\circ\text{C}$ .

The spectra of the transmissivity T and the reflectivity R of the porous Cr film as an IR absorber are measured using the FT-IR equipment. In the reflectivity R measurements the sputtering deposited gold film on the  $\text{SiO}_2$ /mirror polished Si substrate is used as a reference. The incident angle of the focused IR light measured from the surface plane of the sample of the porous Cr film is about  $45^\circ$ . In the transmissivity T measurements the  $\text{SiO}_2$ /mirror polished Si substrate is used as a reference, however in this case the incident IR light is irradiated from the backside rough surface of the reference Si substrate in order to prevent the larger total reflection at the mirror polished Si surface.

In Fig.10 spectra of the transmissivity T (a) and the reflectivity R (b) of the porous Cr film of that in Fig.5 ( $T_s=100^\circ\text{C}$ ) as an IR absorber formed at  $T_s=100^\circ\text{C}$  and underlying metal of Ti as shown in Fig. 2 are shown. The transmissivity T and the reflectivity R in the sample formed at this  $T_s = 100^\circ\text{C}$  are 0.4% and 30% at wavelength  $\lambda = 10\ \mu\text{m}$ , respectively. The total absorption factor at about  $10\ \mu\text{m}$  of IR wavelength is about 69.6% because of having very large reflectivity R in this wavelength.

In Fig.11 the spectra of the transmissivity T (a) and the reflectivity R (b) of the porous Cr film as the IR absorber at  $T_s=400^\circ\text{C}$  and underlying metal of Ti are shown, which is the same sample as that shown in Fig.9.

In this case the deposition conditions are different from

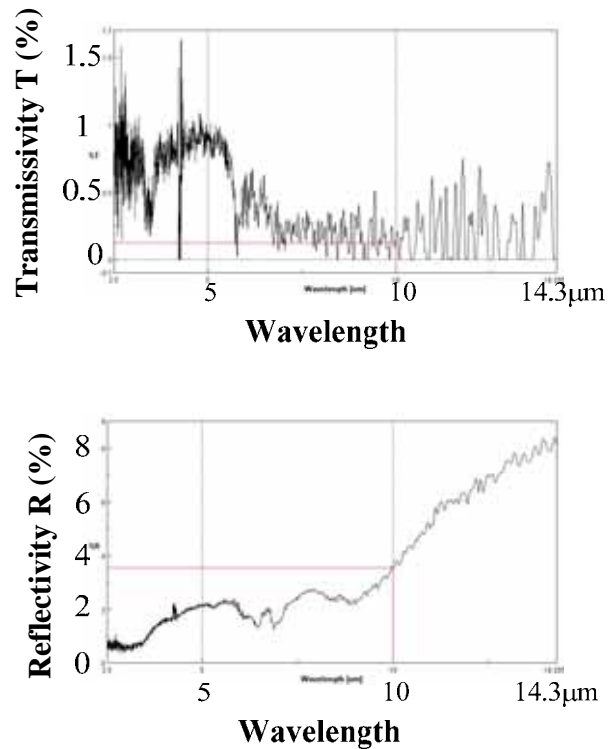


Fig.11 Spectra of the transmissivity T (a) and the reflectivity R (b) of the porous Cr film as an IR absorber at  $T_s=400^\circ\text{C}$ .

that of normal series experiments as shown in Fig 7-10 and next Fig.12 to get the good IR absorption. In this experiment in Fig.11 the Ti deposition time is enlarged to be 15 min. to reduce the transmissivity T, and the film deposition time of Cr-Cu (50:50) layer is also a little enlarged to be 10 min. to increase the IR absorption. The thickness of the Cu removed film of the deposited Cr-Cu (20:80) layer is about 5 $\mu$ m, judging from the SEM image shown in Fig. 9 and this will be the suitable thickness for the IR absorber in the 8-14  $\mu$ m wavelength.

In this porous Cr film formed at Ts=400 $^{\circ}$ C, the transmissivity T and the reflectivity R have been only 0.2 % and 3.6 % at the wavelength of  $\lambda$  =10  $\mu$ m, respectively. Therefore very large total absorption factor of about 96.2%, at near 10  $\mu$ m of IR wavelength is achieved.

In Fig.12 substrate temperature Ts dependences of the reflectivity R of the porous Cr film for various IR wavelengths are shown. In these sample-preparation conditions such as the sputtering deposition time and the sputtering RF power for various sputtering materials are unified to be Ti:3 min. (200W); Cr-Cu (50:50):8 min. (500W); Cr-Cu (20:80):1hr. (500W) as mentioned above.

We can see from these results that as increasing the substrate temperature Ts, the reflectivity R is decreased for every IR wavelength, which directly reflects and leads to the larger total IR absorption factor.

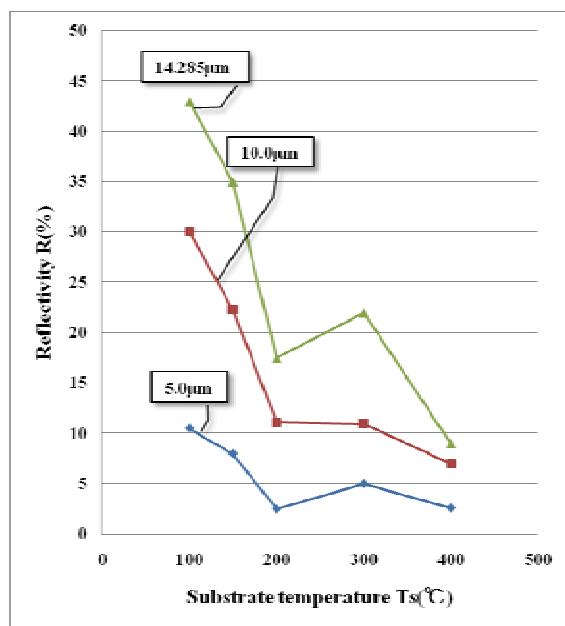


Fig.12 Substrate temperature Ts dependence of the reflectivity R of the porous Cr film (Parameter: IR wavelength).

#### 4 DISCUSSIONS

In Fig.13 an example of enlarged SEM images shown in Fig.7(a) of the mesh structure composed of many needle-

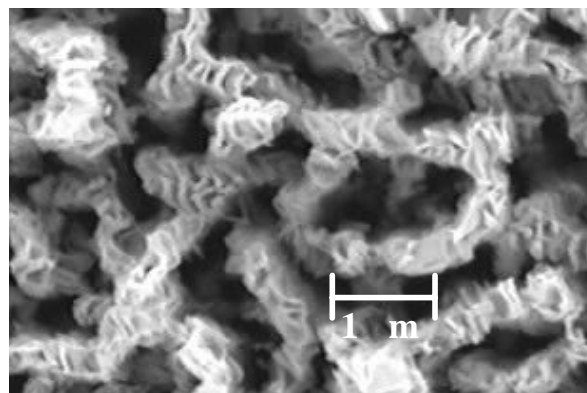


Fig.13 SEM image of the needle-like Cr crystals revealed after Cu etching out from the Cu-Cr (80:20) deposited film formed at Ts=400  $^{\circ}$ C.

like Cr crystals revealed after Cu etching removal from the Cu-Cr (80:20) deposited film at Ts=400  $^{\circ}$ C is shown. We have found that these structures of mesh like and needle-like crystals are already observed in the Cu rich samples sputtering deposited film at Ts=100  $^{\circ}$ C, however lower temperature depositions leads to smaller pore size and larger reflectivity R in the wide range of the IR spectra.

As shown in Fig.9 and in Fig.11 the sample with better characteristics for the IR spectra of 8-14 $\mu$ m wavelength has relatively larger thickness of about 5 $\mu$ m for the Cr-Cu (20:80) film than that of expected one, however, the effective optical thickness must be less than this 5 $\mu$ m because of porous one.

#### 5 CONCLUSIONS

Novel fabrication method of porous Chromium (Cr) film for an infrared (IR) absorber is proposed and total absorption factor above 96.2% at about 10  $\mu$ m, being the peak IR wavelength radiated from near room temperature substance such as the human body temperature, is achieved.

This fabrication method can be applied to the catalytic materials such as the catalytic Pt film because of having nano size pores and easy fabrication.

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