

# Microstructure and Raman spectra of Ag-MgF<sub>2</sub> cermet films

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Ag-MgF<sub>2</sub> cermet films with different Ag fractions were prepared by vacuum evaporation. The microstructure of the films was examined by Raman scattering technique. The surface-enhanced Raman spectrum for MgF<sub>2</sub> molecules in the cermet film strongly suggests the existence of Ag nanoparticles dispersed in MgF<sub>2</sub> matrix. The intensities of the Raman spectra of Ag-MgF<sub>2</sub> cermet films increase with Ag fraction. The enhancement of Raman scattering disappears when Ag content reaches wt.20%. The analyses with the transmission electron microscopy showed that Ag-MgF<sub>2</sub> cermet films are mainly composed of amorphous MgF<sub>2</sub> matrix with embedded faced-center-cubic Ag nanoparticles. It suggests that the percolation threshold should be around wt.20% of Ag content.

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In recent years, there has been much interest in the optical and electrical properties of the cermet films consisted of ceramic matrix and embedded metal nanoparticles. Because of the prospective applications of cermet films as photoelectronics devices based on quantum size effects, thorough and extensive investigations<sup>[1-5]</sup> have been made on cermet films such as Cu-MgF<sub>2</sub>, Ag-SiO<sub>2</sub>, Cu-NaF and Ag-NaF. But Ag-MgF<sub>2</sub> cermet films have scarcely been studied<sup>[6-8]</sup> because of their complicated nature, e.g., the multiphase and the void effect.

Both Ag and MgF<sub>2</sub> are important electrical and optical materials. Obtained results confirm that Ag-MgF<sub>2</sub> cermet films have wide spread applications in producing low-temperature-coefficient film resistors, optical or electromagnetic anti-reflecting layers, and solar energy transform devices etc. In the present study, Ag-MgF<sub>2</sub> cermet films were prepared by vacuum evaporation technique using sintered Ag-MgF<sub>2</sub> mixture granules as evaporant, and the relation between the microstructure and the Raman spectra of the films was examined by Raman scattering technique.

In our experiments, Ag-MgF<sub>2</sub> cermet films were prepared by evaporation in a base vacuum of better than  $4 \times 10^{-3}$  Pa. Similar to Lissberger's method<sup>[1]</sup>, sintered-in-vacuum Ag-MgF<sub>2</sub> mixture was used as evaporant in order to approximate film composition to the evaporant composition. The cermet evaporant was prepared as follows: Ag and MgF<sub>2</sub> powders, both with 99.99% purity and with different weight ratios of 0.5 : 9.5, 1.0 : 9.0, 1.5 : 8.5, 2.0 : 8.0 and 3.0 : 7.0, respectively, were thoroughly mixed, ground and pressed into tablets. Then the tablets were sintered in a vacuum of  $4 \times 10^{-3}$  Pa at 900 °C for 60 minutes. After sintering, the cermet tablets were ground into fine granules to used as evaporant. For optical experimental purpose, cermet films, with thickness ranging from 400 to 500 nm, were deposited at room temperature onto Si(111) wafers.

Raman measurements were carried out in a conventional scattering geometry at room temperature. The spectra were excited by the 514.5 nm wavelength of a 100-mW Ar-ion laser and recorded by a Spex Ramanalog 2M spectrophotometer equipped with a double

monochromator and a photon-counting system. Figure 1 shows the surface-enhanced Raman spectra for Ag-MgF<sub>2</sub> with the Ag weight ratio of 5%, 10%, 15%, 20% and 30%. For comparison, Raman spectra of Ag powder and MgF<sub>2</sub> film are also shown. The Raman modes of MgF<sub>2</sub> molecules at  $1372 \text{ cm}^{-1}$  { $F(2\Sigma) \leftrightarrow E(2\Pi)$ } and  $1431 \text{ cm}^{-1}$  { $E(2\Sigma) \leftrightarrow D(2\Pi)$ } are excited, and the Raman modes of Ag nanoparticles at  $1360$  and  $1600 \text{ cm}^{-1}$  are excited. The Raman peak near  $1130 \text{ cm}^{-1}$  in Fig. 1(c) is due to the interaction between MgF<sub>2</sub> molecules and Ag nanoparticles. The sharp peaks at  $515$ ,  $3080$  and  $3235 \text{ cm}^{-1}$  are typical Raman modes of Si wafers, and the  $515 \text{ cm}^{-1}$  peak was taken as intensity calibration.

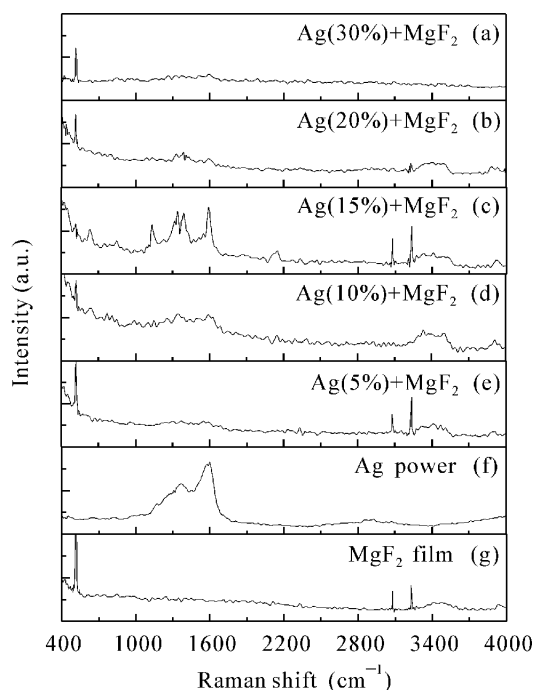


Fig. 1. Raman spectra of MgF<sub>2</sub> film, Ag powder and Ag-MgF<sub>2</sub> cermet films with different Ag fractions: (a) wt.30% Ag; (b) wt.20% Ag; (c) wt.15%Ag; (d) wt.10% Ag; (e) wt.5% Ag; (f) Ag powder and (g) MgF<sub>2</sub> film.

From Fig. 1, we can see that the intensity of the Raman peaks depends on Ag fraction. Furthermore, the intensities are considerably strong for both Ag and  $\text{MgF}_2$ . The intensities of Raman scattering are enhanced by the metal- $\text{MgF}_2$  interaction and the surface plasmons localized in the Ag nanocrystals. Physically, the enhancement mechanism is just the case of surface-enhanced Raman scattering (SERS) of adsorbed molecules on metal surfaces. The protrusions in the form of the islands of Ag nanocrystals dispersed in  $\text{MgF}_2$  matrix have a wide size distribution and the resonant frequency of the surface plasmon strongly depend on the distribution. Therefore, under an excitation with a given wavelength, a localized optical intrinsic phonon mode is resonantly excited.

In Fig. 2, optical absorption spectra of Ag- $\text{MgF}_2$  cermet films with different Ag contents (wt.15%, 20% and 30%) are displayed. The peak around 412 – 417 nm results from the surface plasmon resonance of Ag nanoparticles. The peak is rather broad, because the particle sizes are much smaller than the mean free path of electrons in the bulk metal and in this case electrons are scattered at particle surfaces. Additionally the absorption at 514.5 nm (below wt.20%) is almost unchanged as the size increases. As Ag fraction increases, i.e. the nanoparticle size increased, the peak of Raman spectrum becomes stronger. The causes for the Ag fraction dependence of Raman peak intensity are due to (1) the effect of the surface plasmon enhancement for both Raman modes, (2) the increase in the Ag- $\text{MgF}_2$  interaction for both Raman modes in the electromagnetic interactions between microcrystals for Ag Raman mode, and (3) the sharp decrease of the absorption at 514.5 nm over wt.20%. The electromagnetic interaction between microcrystals also results in the broad distribution of Ag Raman scattering.

When the Ag content reaches wt.20%, the effect of SERS disappears. In order to explore physical reason, we analyzed the TEM bright-field micrograph and the electron diffraction (ED) pattern of the Ag- $\text{MgF}_2$  cermet film<sup>[9]</sup>. The TEM micrographs of wt.15%, 20% and 30% Ag- $\text{MgF}_2$  films are presented in Figs. 3 (a), (b) and (c), respectively. In the TEM micrograph, Ag particles of 10 – 18 nm in size are roughly spherical in shape and embedded in  $\text{MgF}_2$  matrix. No self-gathering effect is observed for Ag particles. The average Ag particle size is about 16 nm. Both the indices of the XRD pattern and

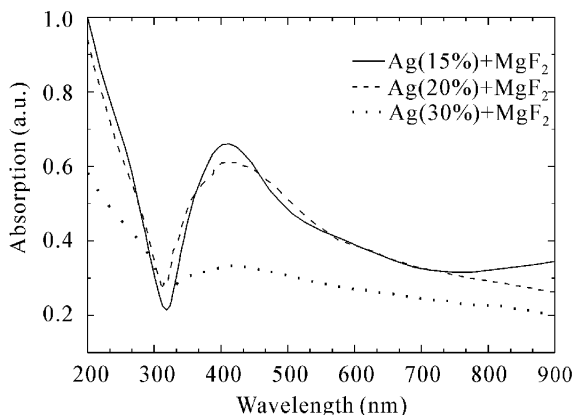


Fig. 2. Optical absorption spectra of nanoparticle Ag- $\text{MgF}_2$  films with different Ag contents.

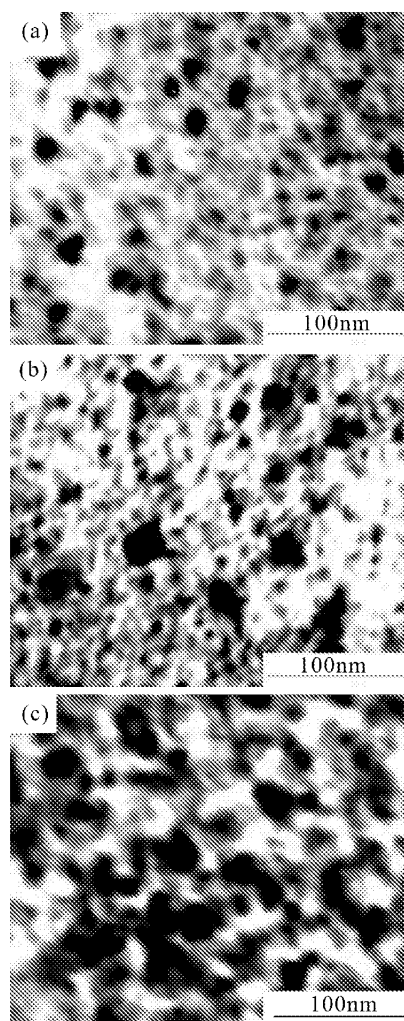


Fig. 3. TEM micrographs of Ag- $\text{MgF}_2$  cermet films with different Ag fractions: (a) wt.15% Ag; (b) wt.20% Ag and (c) wt.30% Ag.

the Debye-Sherrer rings in the ED pattern suggest that the cermet film is mainly composed of the amorphous  $\text{MgF}_2$  matrix and the embedded faced-center-cubic Ag (fcc-Ag) nanoparticles. Therefore, the SERS disappearance is due to sharp decrease of the peak of the surface plasmon resonance caused by the rapid reduction of the ratio of surface to volume of Ag nanoparticles in the Ag- $\text{MgF}_2$  cermet film when the microstructure of Ag content in the matrix changes from isolated nanoparticles to networks formed with contacted nanoparticles. This suggests that the optical percolation threshold should be around wt.20% for Ag content. The result is in a good agreement with the threshold of Ag  $\text{MgF}_2$  film obtained by electrical conductance measurement<sup>[10]</sup>.

The microstructure of the Ag- $\text{MgF}_2$  cermet films with different Ag fractions, prepared by vacuum evaporation, was studied by Raman scattering technique. The surface-enhanced Raman spectrum for  $\text{MgF}_2$  molecules in the films shows the existence of Ag nanoparticles dispersed in  $\text{MgF}_2$  matrix. The intensities of the Raman spectra of Ag- $\text{MgF}_2$  cermet films increase with Ag fraction. However, the surface-enhancement of the Raman scattering disappears when Ag content reaches wt.20%. This re-

sult suggests that the percolation threshold should be around wt.20% for Ag content. The microstructure of the film with this Ag fraction, analyzed by transmission electron microscopy, indeed is mainly consisted of amorphous  $\text{MgF}_2$  matrix with embedded fcc-Ag nanoparticles.

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