

Nanoporous thin film fabrication via magnetron sputtering and O₂ plasma ashing process

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ABSTRACT

We report a new method of fabricating nanoporous catalytic thin films. In the first step, metal-carbon thin films were prepared by reactive magnetron sputtering, using various metallic targets (Au, Ag, Pt, Cu, Ni, Ti) as the metal sources and CH₄ gas as the carbon source. The metal-carbon thin films were then oxidized by an oxygen plasma with a gas mixture of Ar and O₂, and nanoporous metallic (Au, Ag, Pt) or metal-oxide (Cu, Ni, Ti) thin films were obtained by removing the carbon atoms from the metal-carbon thin films. Depending on the film composition and O₂ plasma ashing condition, the calculated porosity varied from 50% to 90%. The new method of fabricating nanoporous thin films is environmentally friendly, applicable to any material and substrate, and easily scalable to large substrate size, wide-opening various application fields including catalysts, sensors, and energy-related electrodes.

Keywords: nanoporous thin film, catalyst, reactive magnetron sputter deposition, plasma ashing, porosity

1 INTRODUCTION

Nanoporous materials with high specific surface areas have much higher reactivity than that of high-density films with the same thickness. Therefore, many studies have been carried out on their application in catalysts [1], sensors [2], surface-enhanced Raman scattering (SERS) [3], and energy-conversion/storage systems [4]. In addition, investigations are actively underway to replace noble metals with relatively inexpensive transition metals for economical production of nanoporous materials.

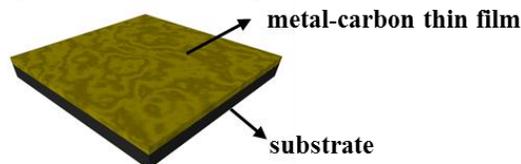
Conventionally, two methods are used for fabricating nanoporous structures: templating [5, 6] and dealloying [7, 8]. In the templating process, desired substances are filled into a template made in the form of the required structure via various processes. When the template is removed, the space previously occupied by the template material becomes pores resulting in a porous structure. However, this method has the disadvantage that separate sequences of complicated processes are required to manufacture and remove the templates. Dealloying is a selective dissolution

process in which an alloy with two or more components with different chemical reactivities is dissolved under the appropriate (electro)chemical environment. The unwanted material is preferentially dissolved and disappears, leaving nano-structure of aming materials. Although the dealloying is a very simple process, harmful acidic and basic solutions must be used inevitably to remove unwanted materials. Moreover, the dissolved metals are wasted [21, 22].

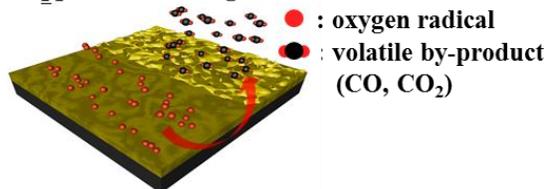
In this study, we developed a simple and stable process for manufacturing nanoporous thin films of various materials (Au, Ag, Pt, Cu, Ni, Ti) through magnetron sputter deposition (pulsed-DC or RF) and subsequent oxygen plasma ashing, without employing a wet process.

2 EXPERIMENTAL

Metal-carbon thin film deposition



O₂ plasma ashing to remove carbon



Nanoporous thin film formation

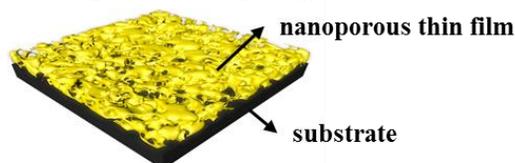


Figure 1: Schematic of the fabrication process of a nanoporous thin film on a substrate.

Figure 1 shows a schematic of the fabrication process of a nanoporous thin film on a glass substrate. An inductively coupled plasma (ICP)-assisted magnetron sputtering device was used in the experiment with Au, Ag, Pt, Cu, Ni and Ti targets as the metal sources. The working pressure was 10 mTorr with the Ar flow rate of 15 sccm, while that of CH₄ gas as the carbon source was varied depending on the target material. A 10 ~ 40 W of pulsed-DC magnetron sputtering power was applied to the sputtering target of Au, Ag and Pt. For Cu, Ni and Ti targets, a 150 ~ 250 W of RF power was used to deposit metal-carbon thin films on the substrates.

The metal-carbon thin films were then subsequently oxidized at room temperature by the O₂ plasma generated by internal ICP antenna at a working pressure of 5 mTorr with O₂ flow rate of 10 sccm and Ar flow rate of 4 sccm. A 150 ~ 400 W of RF power was used to generate O₂ plasma. The highly reactive oxygen species in the O₂ plasma reacted with carbon atoms in the films to form volatile CO and CO₂, which could be easily evacuated during process. In addition, for Cu, Ni and Ti nanoporous thin films, the RF power applied to the ICP antenna, the substrate temperature, and the substrate bias voltage were varied to examine the influence on the porous structure. As a result of exposure to the O₂ plasma, nanoporous thin films with thickness of 150 ~ 400 nm were obtained.

Scanning electron microscopy (SEM; Nova 200, FEI) was used to investigate the morphology of the surface and cross-section of nanoporous thin films. The crystalline structure of the as-deposited metal-carbon thin films and the nanoporous thin films was investigated by using X-ray diffraction (XRD; D/max-2500, Rigaku). Furthermore, X-ray photoelectron spectroscopy (XPS; PHI-5000 Versa Probe, ULVAC-PHI) was used to study the chemical state and composition. In addition, the mass of the nanoporous thin films was measured with a microbalance (Sartorius MSE 3.6P) to indirectly calculate the porosity from the difference between the measured mass of the nanoporous thin film and that of the dense thin film of the same thickness.

3 RESULT AND DISCUSSION

3.1 Nanoporous Au, Ag and Pt thin films

Figure 2 shows the surface and cross-sectional SEM images of the nanoporous Au, Ag, Pt thin films fabricated from ~500 nm thick Au-C, Ag-C and Pt-C thin films and subsequent O₂ plasma ashing for 60 min. The composition of metal-carbon thin films prior to plasma ashing was adjusted by varying the sputtering power. It can be seen that nanoporous structures with randomly interconnected ligaments were formed throughout the samples. For a given plasma ashing condition, the surface diffusion of corresponding element plays a significant role in nanoporous structure formation, markedly influencing the ligament size and porosity. The nanoporous Ag samples exhibits the largest ligament size than Au or Pt samples due

to the higher surface diffusion coefficient of Ag than that of Au or Pt.

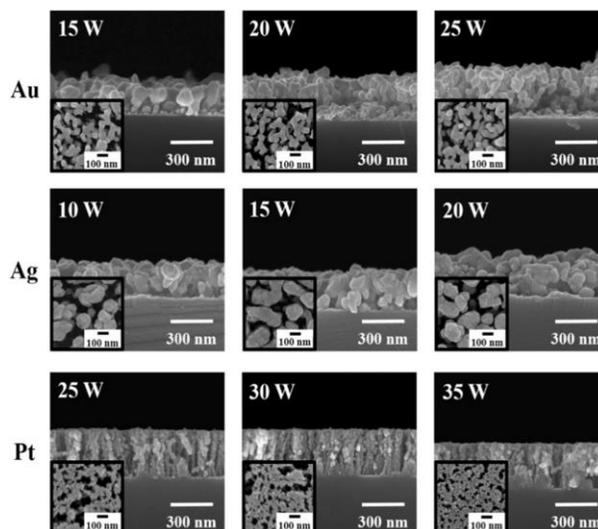


Figure 2: Cross-sectional and surface SEM images of nanoporous Au, Ag and Pt thin films.

The sputtering process, in general, is a highly non-equilibrium process showing a solubility relaxation phenomena, especially for room temperature deposition. However, there is a possibility of forming clusters in the thin film when depositing materials with very low mutual solubility as in noble metal (Au, Ag, Pt)-carbon system. The XRD measurement data for as-deposited noble metal-carbon thin films in Figure 3 shows the polycrystalline cluster formation of noble metals within the as-deposited thin films. Furthermore, the polycrystalline nature was turned out to be preserved even in the nanoporous structure formation after plasma ashing process.

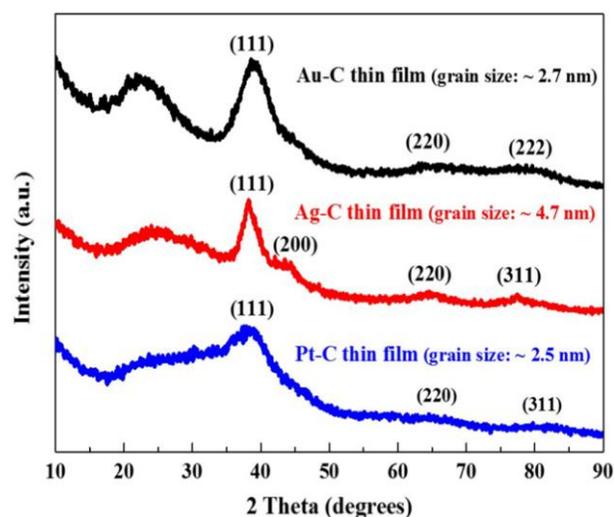


Figure 3: X-ray diffraction pattern of as-deposited Au-C, Ag-C and Pt-C thin films on soda-lime glass substrate.

Figure 4 shows the porosity of nanoporous Au, Ag and Pt thin films for different sputtering power to deposit metal-carbon thin films, measured via microbalance method. The porosity was measured to be 55 ~ 90% and decreased with increasing the sputtering power due to the higher concentration of metals compared to carbon in the as-deposited metal-carbon thin films. In addition, the porosity of Ag nanoporous thin films shows the lowest porosity compared to Au or Pt, resulting from the higher surface diffusion coefficient of Ag than that of Au or Pt.

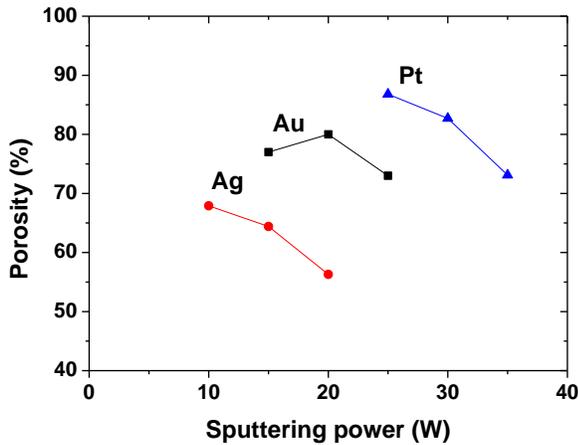


Figure 4: Porosity of nanoporous Au, Ag and Pt thin films by varying the sputtering power.

3.2 Nanoporous Cu, Ni and Ti thin films

Figure 5 shows the cross-sectional and surface SEM images of nanoporous Cu, Ni and Ti thin films. In these samples, reactive RF sputtering with 150 W RF power was used during metal-carbon thin film deposition to prevent arc formation. In addition, CH₄ flow rate was varied from 10 ~ 20 sccm to change the metal to carbon ratio at a fixed Ar flow rate of 15 sccm. The working pressure during thin film deposition was 10 mTorr and the O₂ plasma ashing process was maintained to be the same as in Au, Ag and Pt samples. The nanoporous structure was found to be more developed with increasing the CH₄ flow rate due to the decrease of the metallic elements in the films.

To investigate the chemical states of the nanoporous Cu, Ni and Ti thin films, XPS study was conducted and the results are shown in Figure 6. The weak Cu 2p_{3/2} and Cu 2p_{1/2} satellite peaks indicate that the nanoporous Cu thin film consisted of Cu₂O. The Ni 2p_{3/2} peak and its satellite peak are located at binding energies of ~ 854 eV and ~ 860 eV, respectively, indicating that Ni is in NiO state. In addition, the deconvolution of the Ti 2p spectrum showed that the TiO₂ was the major chemical state and metallic Ti was not observed in the nanoporous Ti thin film.

The crystallographic nature of nanoporous Cu, Ni and Ti oxide thin films was studied with XRD and is shown in Figure 7. In contrast to the nanoporous Au, Ag and Pt thin films, nanoporous Cu, Ni and Ti oxide thin films turned out

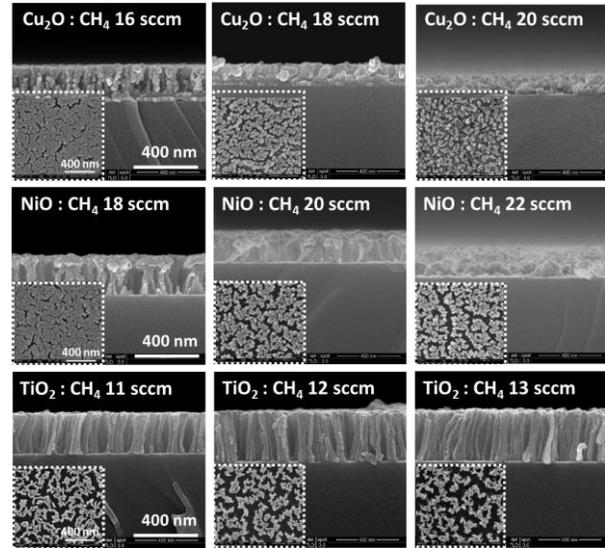


Figure 5: Cross-sectional and surface SEM images of nanoporous Cu, Ni and Ti oxide thin films.

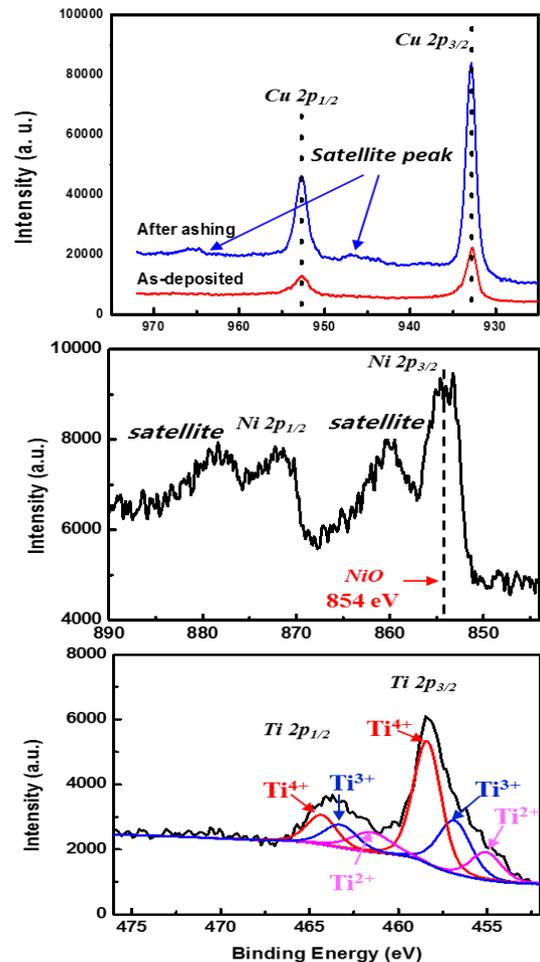


Figure 6: XPS analysis results of nanoporous Cu, Ni and Ti oxide thin films.

to be completely amorphous. It can be considered that the low surface diffusion coefficient of oxide compared to that of metal makes it difficult to be clustered with long-range ordering to give meaningful XRD patterns. A further heat treatment might be necessary to convert the amorphous nanoporous oxide thin films to microcrystalline ones.

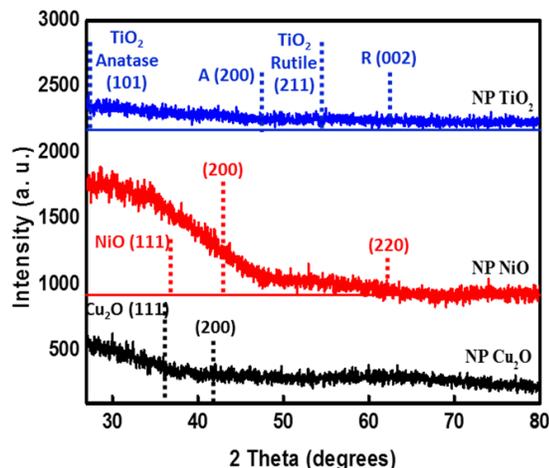


Figure 7: XRD diffraction patterns of nanoporous Cu, Ni and Ti oxide thin films

Figure 8 shows the calculated porosity of nanoporous Cu, Ni and Ti oxide thin films using the microbalance measurement method the same as for nanoporous Au, Ag and Pt samples. It can be seen that nanoporous oxide thin films with porosity of higher than 50% were fabricated and the porosity of each oxide thin film increases with increasing the CH₄ flow rate due to the decreased metal content in the as-deposited metal-carbon thin films. In addition, Cu₂O nanoporous thin films have lower porosity than TiO₂ or NiO, which is attributed to the higher surface diffusion coefficient of Cu₂O compared to that of TiO₂ or NiO, resulting in thicker ligament size and reduced opening between ligaments.

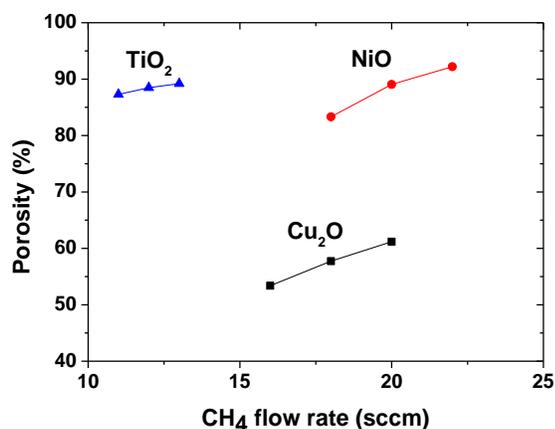


Figure 8: Porosity of nanoporous Cu, Ni and Ti oxide thin films by varying CH₄ flow rate.

4 CONCLUSION

A new method of fabricating nanoporous catalytic thin films has been developed in this study. The metal-carbon thin films were deposited by reactive magnetron sputtering, using various metallic targets (Au, Ag, Pt, Cu, Ni, Ti) and CH₄ gas as the carbon source. Subsequently, the metal-carbon thin films were oxidized by an O₂ plasma, resulting in the formation of nanoporous metallic (Au, Ag, Pt) or metal-oxide (Cu, Ni, Ti) thin films by selectively removing the carbon atoms in the films. The new method of fabricating nanoporous thin films is environmentally friendly, applicable to any material and substrate, and easily scalable to large substrate size. The method can be applied in various application fields including catalysts, sensors, and energy-related electrodes.

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