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Technical Review

Research and Development of Functional Thin Films Utilizing Sol-Gel Technology

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Abstract

Inorganic/organic hybrid films consisting of inorganic and organic species at the nanoscale have been studied. By controlling the structure, molecular weight, and reaction conditions of the precursors using sol-gel technology, flexible stainless steel foils with functional films such as heat resistance, insulation, and planarization have been developed. In the future, our company will propose new products that meet the stringent requirements of electronic device and semiconductor manufacturing processes while aiming for even higher functionality.

1. Introduction

Inorganic/organic hybrid materials are composed of inorganic and organic species at the nanoscale. These materials are expected to find applications in diverse fields—including coatings, optical and electronic materials, and medical devices—due to their capacity to exhibit novel functionalities by integrating the properties of both inorganic and organic constituents.[1] In general, inorganic materials possess excellent mechanical and thermal stability owing to their chemical composition, structure, crystallinity, etc. Conversely, organic materials have functional properties such as optical, electrical, and chemical properties, as well as hydrophilicity control, due to their diverse molecular structures. Inorganic/organic hybrid materials, in which both or at least one of the inorganic and organic materials are integrated at the nanoscale, are expected to exhibit not merely the sum of inorganic and organic species, but even the unique properties of inorganic/organic hybrid materials.

The sol-gel method is a representative technique for integrating inorganic and organic species on the nanometer scale. The sol-gel method enables the formation of an inorganic framework consisting of metal-oxygen (...M-O-M...) bonds at low temperature, and allows the incorporation of organic species into the inorganic framework at the molecular level.[2, 3] Furthermore, various morphologies, such as bulk materials, films, particles, and fibers, can be obtained from solutions via the sol-gel method making it applicable to a wide range of product forms. Research on inorganic/organic hybrid materials using the sol-gel method commenced around 1985 under the names of ORMOSILs[4] (Organically Modified Silicates) and Ceramers,[5] and numerous researchers have since contributed to their development.

In addition to conducting research on ceramic material synthesis via the sol-gel method, Nippon Steel Corporation participated in the national project “Research and Development of Synergistic Ceramics,” initiated in 1994 by the Industrial Science and Technology Research and Development System of the former Ministry of International Trade and Industry. This project aimed to develop novel materials that leverage the synergistic effects of inorganic and organic properties.[6] In this project, hybrid materials exhibiting flexibility—uncharacteristic of conventional ceramics—were discovered by incorporating organic components into the inorganic network of ceramic materials, which are typically hard and brittle. Advanced materials with not only mechanical properties, but also chemical functionalities such as optical, electromagnetic, and selective adsorption were developed through precise control of chemical reactions based on composition and synthesis conditions, coupled with structural design. Even after the completion of this project, we have continued to develop and accumulate technologies that exploit the advantages of the sol-gel method (hereinafter referred to as sol-gel technology) to enable diverse applications.

In this review, we focused on the application of inorganic/organic hybrid materials with flexible properties discovered by Nippon Steel, especially on thin film fabrication, which offers the broadest range of applications. We also outline the design strategies for coating solutions using sol-gel technology and the characterization of functional thin films derived from the designed coating solutions.

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2. Preparation of Inorganic/Organic Hybrid Films Using Sol-Gel Technology

In the sol-gel method, metal-organic compounds, mainly metal alkoxides $M(OR)_n$ (M=metal, R=organic group), are used as precursors. The metal alkoxide undergoes a hydrolysis reaction (1) and polycondensation reaction (2) involving dehydration and dealcoholization at approximately room temperature to form an inorganic framework consisting of M-O-M bonds.[7]

$$\text{M-OR} + H_2O \rightarrow \text{M-OH} + \text{ROH} \qquad (1)$$

$$\text{M-OH} + \text{HO-M} \rightarrow \text{M-O-M} + H_2O \qquad (2)$$

The above reaction equations represent the stoichiometric scheme of the reactions involving metal alkoxides. In other words, polycondensation is a complex process because the reaction does not necessarily start after complete hydrolysis; rather, it may proceed immediately after partial hydrolysis of the metal alkoxide. The ratio of the hydrolysis reaction rate to the polycondensation reaction rate varies depending on the reaction conditions in the solution (type of metal alkoxide and solvent, solution pH, water content, temperature, etc.). Therefore, controlling these reactions is essential for tailoring the morphology of the composite with organic materials, particles, and thin films.

Through its previous research and development, Nippon Steel has established a method for incorporating organic species and controlling thin-film morphology.[8] For example, tetramethoxysilane ($Si(OCH_3)_4$) and methyltriethoxysilane ($SiCH_3(OC_2H_5)_3$) were used as primary precursors, mixed in organic solvents, and hydrolysis and polycondensation of each alkoxysilane were adjusted by catalysts. Consequently, an inorganic/organic hybrid polymer was formed, in which tetramethoxysilane and methyltriethoxysilane were interconnected via siloxane (Si-O-Si) bonds. Subsequently, the polycondensation reaction progressed further during coating and drying, resulting in a thin film with a methyl group-modified siloxane structure, as shown in **Fig. 1**, was obtained.

3. Developed Products Using Inorganic/Organic Hybrid Films and Their Properties

Recently, research and development of flexible electronic devices, such as smartwatches worn on the wrist and IoT sensors applied to curved surfaces, have become increasingly active with the advent of 5G. Conventional electronic devices are typically fabricated on insulating glass substrates. However, as glass is brittle and hard, it is difficult to use a glass substrate for flexible electronic devices. On the other hand, organic resin films, although flexible, exhibit inferior heat resistance and gas barrier properties. To address these limitations, Nippon Steel has promoted research and development of stainless steel foils which offer excellent heat resistance and chemical stability for use as flexible substrates.[9] Stainless steel foils present challenges such as electrical conductivity and surface roughness; however, they can serve as flexible substrates with insulation and flatness when coated with an inorganic/organic hybrid film. For more information, see another article. The New Materials Development Center of Nippon Steel Chemical & Material Co., Ltd. and collaborators have developed the Roll-to-Roll technique using ultra-thin stainless steel foils for continuous film deposition and heat-treatment. It is crucial to control the molecular weight and reactivity of the inorganic/organic hybrid polymers in the coating solution to achieve the desired properties with short heat-treatment times and enable mass production using the Roll-to-Roll process.

3.1 Insulation evaluation of stainless steel foil with film for heat-resistant applications[8]

Reducing the amount of organic species introduced into an inorganic/organic hybrid brings its properties closer to ceramics, which exhibit excellent heat resistance. For example, a coating solution was prepared by mixing tetramethoxysilane and methyltriethoxysilane. A stainless steel foil was coated using a bar coater with the coating solution, dried at 160°C for 1 minute, and then heat-treated in nitrogen at 400°C for 30 minutes. **Figure 2** shows the relationship between the thickness of the cured film and insulation resistance. The stainless steel foil was mirror finished SUS444 ferritic stainless steel foil manufactured by Nippon Steel Chemical & Material with a thickness of 80 μm and a roughness of Ra < 0.03 μm.

Insulation resistance was measured by determination from the minute current flowing through the foil at an applied voltage of 60 V, using a 1 mm-diameter Pt upper electrode and the stainless steel foil as the lower electrode. As a result, an insulation resistance of 1×10^9 $\Omega \cdot cm^2$ or higher was obtained for a film thickness of approximately 1 μm or more. However, at a film thickness of 1.5 μm, cracks oc-

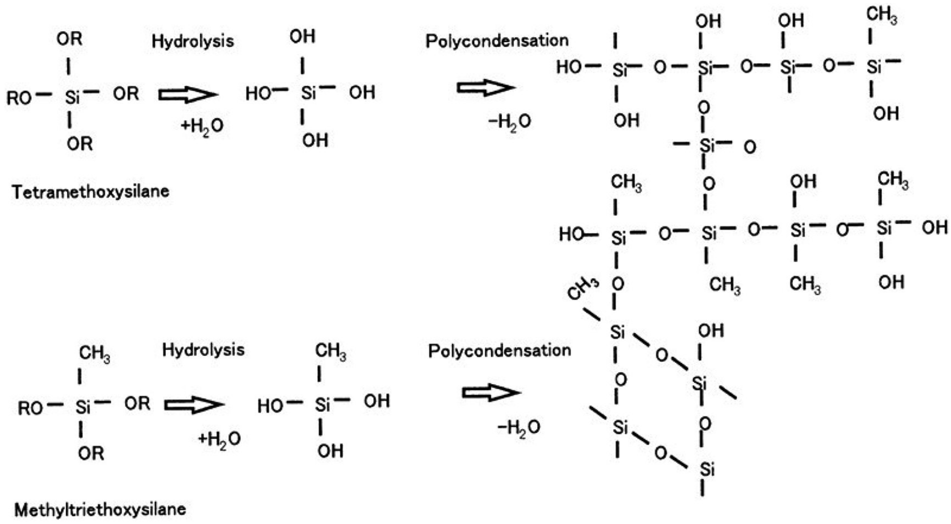

Fig. 1 Synthesis of coating solution

curred in the film, resulting in short-circuiting between the electrodes. For films thinner than 1 μm, microscopic protrusions on the stainless steel foil surface were considered to cause defects leading to low resistance. These findings demonstrate that sufficient insulation can be ensured by appropriately controlling the film thickness.

The dried films were then heat-treated at 300°C or 400°C under a nitrogen atmosphere. **Figure 3** shows the relationship between heat-treatment temperature and time and insulation resistance of each cured film. Higher insulation resistance was obtained at 400°C than at 300°C. Furthermore, at 400°C, even when the heat-treatment time was reduced to 1 minute, the insulation resistance was nearly equivalent to that of the cured film treated for 30 minutes. This result indicated that sufficient insulation resistance could be achieved even with short heat-treatment times assuming roll-to-roll processing.

3.2 Planarity evaluation of stainless steel foil with film for electronic device applications[9–11]

Stainless steel foil is manufactured through a rolling process, which produces rolling striations on the surface. Since each layer that constitutes an electronic device is on the order of nanometers in thickness, the surface of the stainless steel foil must exhibit planarity comparable to that of glass substrates to prevent short-circuiting between layers. To meet the required properties of inorganic/organic hybrid films with superior planarity and rapid drying and heat-treatment, the structure and molecular weight of the hybrid polymers in the coating solution were carefully designed. The dried film was obtained on the stainless steel foil by spin-coating with the coating solution, and the cured film was produced by heat-treatment in a clean oven.

Figure 4 shows SEM (Scanning Electron Microscope) images of (a) mirror-finished SUS444 ferritic stainless steel foil manufactured by Nippon Steel Chemical & Material with a thickness of 50 μm and (b) 3–4 μm-thick planarization film formed on it. In the case of (a), rolling striations parallel to the rolling direction were clearly observed on the mirror-finished surface. After the film was formed on SUS444, the surface appeared smooth, without rolling striations. AFM (Atomic Force Microscope) images of the surface after the planarization film formation are shown in **Fig. 5**. Surface roughness was reduced from 78.2 nm to 8.9 nm for Rmax and from 6.2 nm to 0.6 nm for Ra, achieving Ra values equivalent to those of glass substrates.

4. Future Prospects

Nippon Steel has developed inorganic/organic hybrid materials with various properties, including flexibility, by sol-gel technology to control the structure, molecular weight, and reaction conditions of the precursors. Additionally, we have succeeded in achieving the desired functionality in coated films even with short heat-treatment times in a roll-to-roll system for mass production. In the future, we aim to further enhance heat resistance, insulation, planarity, and other functionalities, and propose the development of new products that meet the stringent requirements of electronic devices and semiconductor manufacturing processes.

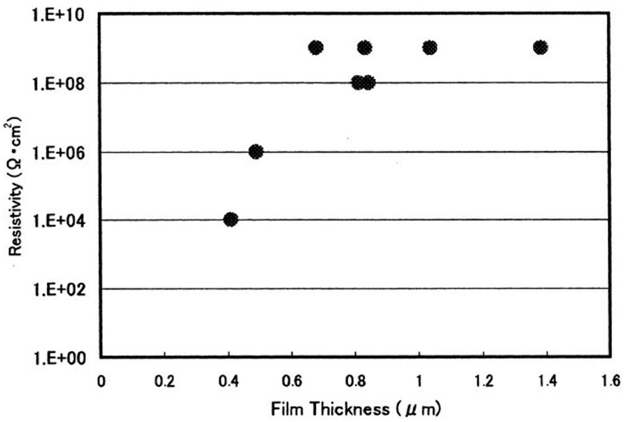

Fig. 2 Relationship between film thickness and resistivity

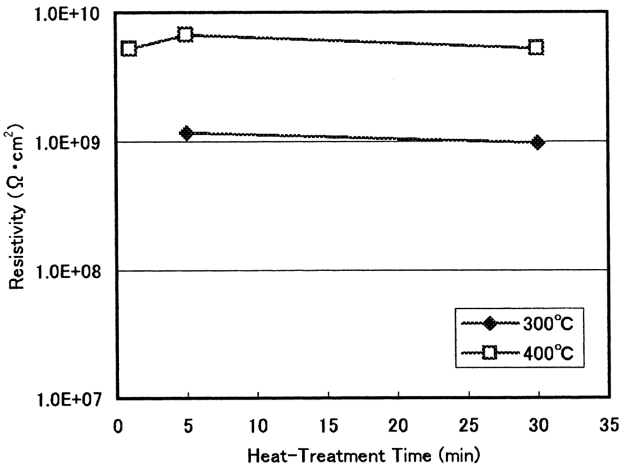

Fig. 3 Effect of heat-treatment temperature and time on resistance

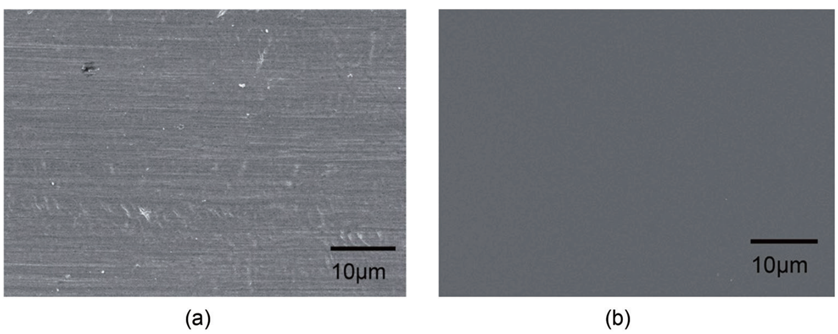

Fig. 4 SEM images of SUS444 (a) before and (b) after planarization

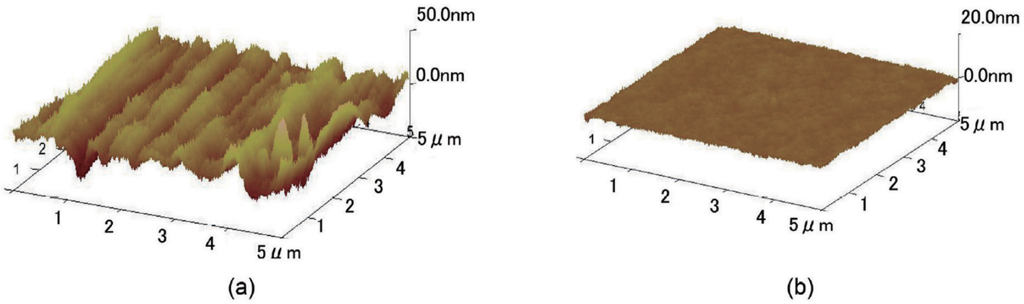

Fig. 5 AFM images of SUS444 (a) before planarization and (b) after planarization

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