Research on the High-Strength Coating Preparation Methodology based on Acid Catalytic and Sol-Gel Method

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Abstract. In this paper, we conduct research on the high-strength coating preparation methodology based on acid catalytic and Sol-Gel method. This method has been widely used in the preparation of various functional thin film, film and protective film structure, etc. As a result of sol gel process continuously broaden the application field, this method has been more and more get the favor of people. Compared with other traditional preparation methods of inorganic material, sol-gel process has many characteristics. To adjust the solution acidity and add a small amount of acid or alkali can have the effect of catalyst, its reaction process on sol to gel and gel structure may also be affected. Our research analyze the topic theoretically and numerically which is meaningful.

Keywords: High-Strength; Sol-Gel Method; Coating Preparation; Acid Catalytic.

Introduction

The Sol-gel method is considered to be potential preparation high laser damage threshold of optical antireflection thin film method. Because of the thin film production costs low, simple coating, easy cleaning, convenient for large area film and optical performance is good wait for a series of advantages and people's attention. When used as a single-layer coating, because the film is formed by nanoparticles accumulation, and therefore is porous, easy absorption of moisture, poor stability and mechanical properties are in use process prone to film transmittance downward and laser damage threshold. Therefore conducted a large number of modified research, the research results show that in the process of preparing silica suspension colloid, doped polyvinyl alcohol can improve film laser damage resistance of the mixed silicone adhesive can effectively improve the mechanical properties of the film and the porous silicon dioxide thin film on ammonia atmosphere or atmosphere after processing, the optical properties of film layer basic remains the same while its mechanical properties can be improved. Focus in the study of the modification and however, we have mainly focused on film properties and the influential factors of processing property of coating modification solution stability study reported less. High-strength coating with low density, low dielectric constant, adjustable refractive index, high thermal stability, good wear resistance and other characteristics, in optical and optoelectronic materials, sensors, filters, auto glass and the microelectronics IC has the wide range of applications. The simplest coating is single layer film and it is plated in optical element of thin film on the surface of a layer of low refractive index [1]. Many optical materials and devices need to be in relatively poor conditions for outdoor use, the coating on the optical materials subjected to the wind rain, so this type of optical material for environmental damage resistance requirements of the coating is very high and the needs is urgent, the higher the strength of the film.

The general high-strength coating preparation methodologies could be summarized as the follows. (1) The physical vapor deposition method. Physical vapor deposition method contains material of gasification, sublimation and coagulation process, the process in non-equilibrium state, can be prepared in the
equilibrium state does not exist. Use of evaporation materials or sputtering materials for the preparation of thin film, at the same time using resistance heating electron beam and ion beam or a laser beam, the new energy as the general source of evaporation or sputter source. (2) The atomic layer deposition. Atomic layer deposition is one of the depositions of thin film prepared by the method, it through constant since the general restrictions of interface reaction to form solid thin film materials. The advantages of atomic layer deposition include can undertake single atomic layer deposition, atomic layer thickness accuracy is achieved to form film, thus we can get on a large area of substrate thickness uniformity of film which can control the film thickness by controlling the reaction cycles, which can control the growth and ultrathin membrane [2]. (3) Hydrolyzation precipitation. The film after drying, satin, dehydration, crystallization can be formed TiO₂ crystal film. By using this method, the TiO₂ membrane materials is cheap, layer of the membrane structure is evener, adhesion is better. But its preparation for TiOSO₄ concentration in the process of pH and temperature conditions needs to be more tightly controlled. Because these conditions will directly affect and influence the particle size, distribution uniformity, membrane layer density and adhesion. (4) Sol-Gel Method. In general, easy to hydrolysis of metal compounds, such as chloride, nitrate, and metal are suitable for this process. In this paper, that is the way that the preparation of silicon dioxide thin film. In the following figure one, we demonstrate the general process of the Sol-Gel method visually.

Figure 1. The Demonstration of the General Process of the Sol-Gel Method

In this paper, we conduct research on the high-strength coating preparation methodology based on acid catalytic and Sol-Gel method. Physical method of the preparation of optical thin film has good stability and surface properties, but its drawback is that film stress is higher and defect is more in film laser damage threshold is low. Chemical coating technology development especially the application of sol gel technology
provides a new way to solve these problems and challenges.

The Proposed Methodology and Approach

The Principles of Acid Catalytic. The preparation of the coating is the precondition of the research and application, to obtain uniform diameter and less with high purity and structure defects of coating is the basis of the research and application research on its performance. Catalytic growth in the coating of metal elements will have metal residual impurities, which will limit coating in the electronics and pharmaceutical applications, while selecting nonmetal catalyst can overcome this problem, to expand the application range of the coating. Under the condition of acid catalysis of protons is the first step, is very fast. In this way, the electron cloud of Si atoms will be attracted the protonation O atom, make Si into more electrophilic, more acceptable molecule's attack [3]. Molecular attack from the back and get some electropositive, and on the alkoxy of the protonation of electro-positivity is relatively less, making it a good leaving group. Substitute for the transition state with alcohol and from the end, at the same time Si tetrahedron Walden flip.

According to the hydrolysis mechanism of hydrolysis velocity varies with Si atoms alkyl group base R low space steric hindrance and significant to speed up. On the power supply of alkyl groups can make the transition state of electro-positivity is more stable, so can also improve the hydrolysis speed, but as a result of Si in transition state electro-positivity is small, so the power supply of alkyl influence on hydrolysis rate is not very big. Hydrogen bonding interaction between solvent and alkoxy anion may be beneficial to the reaction. Hydroxyl and silicon triol first step reversible fast reaction, generate silanol anion. In this way, the polymerization is first order reaction, for hydroxyl silicon for three alcohols is second order reaction. Probably because of the space steric hindrance, two of the siloxane in the shorter reactions times no further condensation. Because the Si atoms in the transition state has had a real negative charge, so coordination group induction effect and space steric effect has equally impact. In the figure two, we illustrate the acid catalyzed hydrolysis reaction mechanism.

![Figure 2. The Demonstration of the Acid Catalyzed Hydrolysis Reaction Mechanism](image)

The Proposed Sol-Gel Method. Of the development decreased membrane is prepared by using some easy hydrolysis in some of the solvent metal compounds or alkoxy compounds react with water, through the hydrolysis and poly-condensation process to form a sol, then the sol coating in the liquid film is formed on the base, after gelation by subsequent heat treatment gel film can be transformed into functional or more amorphous film. Solution or sol in the polymer structure, the water volume, viscosity, speed, rotation speed and time factors such as the thickness of single layer film and microstructure. In SiO$_2$ sol reaction system, the hydrolysis reaction is double molecular nucleophilic substitution reaction, generation five coordination of intermediates or transition state. In acidic conditions, the reaction mechanism for the electrophilic reaction and in alkaline condition, the reaction of nucleophilic reaction. It is the general condition of acid and alkali catalysis accelerates or defers the electrophilic and nucleophilic reaction. Under the condition of acid catalysis, an alkoxy in silicon alkoxide was quickly first protons and the charge density on the silicon atoms to the groups of protons and migration which make it more accessible to water molecules.

The rule of law to the surface of the silica coating contains a lot of polar hydroxyl, easy
adsorption in the environment of water, organic pollutants and results in the decrease of light transmittance, short service life. In order to prolong the service life of the silica coating, people make a lot of work, mainly concentrated in the colloid introduced in the introduction of hydrophobic groups in silicon methyl silicone, can greatly improve the hydrophobic membrane layer, but the improvement of membrane layer oleo-phobic property without help. The poly-condensation reaction is most likely to occur in the protonation of monomer or macromolecular oligomers between end groups, the resulting polymer crosslinking degree is not high, generally for approximation of the linear polymer, and the gel formed by their further crosslinking system skeleton. In alkaline condition, the formation of hydroxyl/hydroxyl anion and proton silane alcohol-based is better nucleophilic reagent. Very few people use post-processing method to improve the hydrophobic oleo-phobic property of coating, it is generally believed that treatment can reduce the optical properties of film layer. In the following formula, we illustrate the process of the steps.

\[
\text{Si(OR)}_4 + xH_2O \rightarrow \text{Si(OR)}_x(OH)_{4-x} + xROH \quad (x = 1 - 4)
\]

\[
= \text{Si} - \text{OR} + \text{RO} - \text{Si} \rightleftharpoons \text{Si} - \text{O} - \text{Si} + \text{R} - \text{OR}
\]

\[
= \text{Si} - \text{OR} + \text{HO} - \text{Si} \rightleftharpoons \text{Si} - \text{O} - \text{Si} + \text{R} - \text{OH}
\]

\[
= \text{Si} - \text{OH} + \text{HO} - \text{Si} \rightleftharpoons \text{Si} - \text{O} - \text{Si} \equiv +\text{H}_2\text{O}
\]

Before the body in the process of hydrolysis and poly-condensation reaction, the size of the aerosol particles and crosslinking degree major is mainly by the water in the solution pH and molar ratio of precursor solution. The mechanisms of hydrolysis and poly-condensation reaction process vary with the pH value. Under the condition of alkali as the catalyst, as a result of OH- to the protonation effect, can produce stronger nucleophilic agent, thus the poly-condensation reaction has a promoting effect; And under the condition of acid as a catalyst, can accelerate the hydrolysis reaction, this is mainly because acid can be provided to the proton has a negative price -OR groups, from the proton transfer process in the transition state, formed to water ionic groups at the same time.

\[
\text{Si(OCH}_3)_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH}
\]

Water and alkoxy compounds in the hydrolysis process ARE not easy to compatible, so choose a suitable solvent can not only achieve the goal of soluble precursor, but also can extend the miscibility between reactants. Alcohol is a common solvent, increase the amount of alcohol can not only make the formation of the polymer network become sparse, and can be diluted solution, the gelation time, on the other hand, the sol is likely to happen gelation. In addition, the solvent also affects the general microstructure of thin film, after alcohol volatile will leave a hole in the film, so change the amount of alcohol can effectively adjust the film in the pore size and porosity and the dosage of the solvent and affect the size of the sol particles thus affect the uniformity of the film.

The Numerical Simulation and Experiment. Hydrolysis and poly-condensation reaction of ethyl silicate is homogeneous solution into the root cause of the sol. Therefore, control of hydrolysis and poly-condensation reaction conditions is particularly important. Ammonia dosage for membrane layer anti-reflection rate of peak and peak wavelength anti-reflection effect is not big, but the impact each step reaction speed. In the following figure, we illustrate the simulation result.
Conclusion

In this paper, we conduct research on the high-strength coating preparation methodology based on acid catalytic and Sol-Gel method. The basic principle of preparation of thin-film coating is: will the metal alkoxide or inorganic salt as precursor, dissolved in solvent to form homogeneous solution, solute and solvent hydrolysis or alcoholysis reaction, reaction products gathered into several about nanometer particles and the formation of sol, again with sol as raw material for a variety of base material coating processing, sol membrane after gelation and drying treatment to get dry gel membrane, finally in a certain temperature annealing is to get the required coating. Our research provides novel paradigm of the design and implementation of high-strength coating preparation methodology which will be meaningful and necessary for the chemistry research community.

References

