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Research on Photolithography Technology and Photoresist Materials in Chip Manufacturing

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Abstract. As semiconductor manufacturing technology evolves, lithography, a core process, faces the dual challenges of achieving higher resolution and smaller feature sizes. This paper explores the fundamental principles and development history of lithography technology, as well as its bottlenecks. It also delves into the differences between conventional organic and novel inorganic photoresists, with a particular emphasis on the unique advantages and reaction mechanisms of novel inorganic photoresists in Extreme Ultraviolet (EUV) lithography. Furthermore, it systematically investigates the photochemical reaction mechanisms of photoresists in EUV and Deep Ultraviolet (DUV) lithography, including processes such as light absorption, photoionization, molecular dissociation, and fragment release. The effects of key factors like photoresist composition, structure, exposure dose, power, and photoresist thickness on the reaction characteristics are thoroughly examined. In addition, it proposes optimization directions for photoresist performance and experimental validation methods, aiming to promote the development of semiconductor manufacturing technology towards higher precision and eco-friendliness.

Keywords: Lithography technology; Photoresist; EUV lithography; DUV lithography.

1. Introduction

The microelectronics industry has witnessed a rapid growth in the demand for the miniaturization of semiconductor devices. Lithography technology is a very crucial process in semiconductor manufacturing, playing a key role in determining the integration and performance of chips. With the continuous development of light sources, the feature dimensions of semiconductor devices are becoming smaller and smaller. However, when the size of the device is approaching its physical limit, photolithography technology is confronted with challenges it has never encountered before. All the chemical reaction characteristics of photoresist materials have a significant impact on the quality and precision of the photolithography patterns, and have now become a key factor in addressing these challenges.

According to the research of Zhang et al., photolithography technology has evolved significantly, with each iteration bringing about a reduction in feature sizes [1]. However, the advancement of this technology has also led to new challenges, for instance, traditional photoresists have certain limitations in achieving higher resolution and smaller feature sizes.

The demand for higher resolution in the semiconductor manufacturing industry is constantly increasing. This situation clearly highlights the limitations of traditional photoresists. As a result, finding new photoresist materials and exploring their reaction mechanisms has become a very urgent issue. This article analyzes the differences between traditional organic photoresists and new inorganic photoresists. The advantages of the new inorganic photoresist in EUV lithography and its reaction mechanism were analyzed in detail. The photochemical reaction mechanism of photoresists in EUV and DUV lithography was also discussed, which includes situations such as light absorption, photoionization, molecular dissociation, and fragment release. Meanwhile, the influences of factors such as the composition, structure, irradiation dose, power, and thickness of photoresists on the reaction characteristics were studied.

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The research content includes: analyzing the basic principles and development history of lithography technology and its bottlenecks; comparing the characteristics of conventional organic and novel inorganic photoresists; studying the photochemical reaction mechanisms of photoresists in EUV and DUV lithography; and proposing optimization directions for photoresist performance and experimental validation methods.

Based on the research of Grace H. Ho et al, the photochemical reactions of photoresists play a crucial role in determining the quality of lithography patterns. Their study revealed the complex reaction mechanisms of photoresists under different lithography conditions, providing valuable insights for this research [2]. Luo, Yan et al. reviewed the latest advances in metal-oxide-based photoresists, covering various novel materials like tin-oxo-cage compounds, zinc-oxide cluster photoresists, and HfO_2- and ZrO_2-based nanoparticle photoresists. Their characteristics, reaction mechanisms, and applications in lithography were discussed, offering broad ideas for this study on new photoresist materials [3]. E. Hendrickx et al. centered on EUV lithography's manufacturing performance, analyzed the current state and challenges of photoresists in high-resolution lithography, explored keys to boosting EUV photoresist performance and its future path, offering vital insights for this study on EUV photoresist optimization [4]. Z. Wang et al. deeply studied hybrid - nanoparticle photoresists' mechanisms, especially the impact of particle size on photopatterning. They highlighted nanoparticle photoresists' potential in boosting lithography resolution and performance, offering useful references for this study to explore new photoresist materials' reaction mechanisms and optimization directions [5].

This paper aims to promote the development of semiconductor manufacturing technology towards higher precision and environmental protection. By exploring the basic principles, development history, and bottlenecks of lithography technology, this paper provides some guidance for the future development of lithography technology. This paper analyzes different photoresist materials, their characteristics, and the reaction mechanisms of new inorganic photoresists in EUV lithography. And the direction for optimizing the performance of photoresist and the methods for experimental verification were proposed. This research holds crucial theoretical and practical significance. It enables us to understand photolithography technology and reaction mechanisms, and also allows for the development of new photoresist materials, which can enhance the precision and efficiency of the photolithography process. The potential contribution of this research lies in the development of new photoresist materials with higher resolution and lower environmental impact, thereby overcoming the limitations of traditional photoresists. It can also meet the future demand for smaller feature sizes in semiconductor manufacturing.

According to the research of Hongzhu Xi et al, novel inorganic photoresists based on phase-change materials like $Ge_2Sb_{1.5}Bi_{0.5}Te_5$ (GSbTe) exhibit unique advantages in EUV lithography [6]. Their study demonstrated the dual positive and negative resist characteristics of GSbTe, providing new ideas for photoresist optimization. This research builds upon their findings to further explore the reaction mechanisms and optimization directions of novel inorganic photoresists.

In summary, the research conducted in this article is beneficial. It can help advance photolithography technology, promote the development of photoresist materials, and also provide new perspectives and methods for the development of semiconductor manufacturing technology.

2. Fundamental Principles of Lithography Technology

Lithography technology is a core process in semiconductor manufacturing for transferring microscopic patterns from a mask to a silicon wafer. It uses the imaging and interference properties of light to control exposure areas and doses, causing chemical changes in photoresists to form patterns. Modern lithography technology has evolved from visible light sources (g-line 436nm, i-line 365nm) to deep ultraviolet (KrF excimer laser 248nm, ArF excimer laser 193nm), and now to extreme ultraviolet (EUV, 13.5nm) to achieve higher resolution and smaller feature sizes. The lithography resolution is described by the Rayleigh equation, where R is the resolution, k_1 is the Rayleigh constant,

λ is the wavelength of the light source, and NA is the numerical aperture of the optical system. Efforts to improve resolution focus on reducing the Rayleigh constant, shortening the wavelength, and increasing the numerical aperture. EUV lithography emerged to meet these demands.

The lithography process involves multiple steps: cleaning and pre-treating the silicon wafer to remove surface contaminants and enhance photoresist adhesion; spin-coating the photoresist and soft-baking to remove solvents; selectively exposing the photoresist through a mask to induce chemical reactions; developing to remove exposed (positive resist) or unexposed (negative resist) photoresist to form patterns; and transferring the pattern to the silicon wafer film layer through etching[1]. Each step must be precisely controlled to ensure pattern accuracy and quality. The traditional lithography process usually consists of spin coating, post-application bake (PAB), exposure, post-exposure bake (PEB), and development.

In the field of lithography technology, shortening the wavelength of the light source is actually a very crucial factor in achieving high resolution. From the initial ultraviolet light to the later deep ultraviolet light, and now to the EUV lithography technology in use, each upgrade of lithography technology has brought particularly significant breakthroughs to this field. Extreme ultraviolet lithography technology has an extremely short wavelength. This extremely short wavelength can achieve sub-nanometer-level feature dimensions, thus enabling devices to develop in the direction of miniaturization. However, EUV lithography technology also faces some challenges, such as issues with the power of the light source, obstacles in the design of the optical system, and challenges related to the performance of the photoresist. The chemical reaction characteristics exhibited by the photoresist under EUV radiation have a very crucial impact on the final presentation of lithography.

3. Characteristics of Photoresist Materials

Photoresist is a particularly crucial core material in photolithography technology. Its performance will affect the quality and resolution of photolithography. Photoresist can mainly be divided into two categories: one is the traditional organic photoresist, and the other is the new inorganic photoresist.

3.1. Conventional Organic Photoresists

Traditional organic photoresists use organic polymers as the substrate and rely on the chemical amplification effect to carry out pattern transfer work. These traditional organic photoresists have wide applications in the field of deep ultraviolet lithography. Their main components include matrix resins, photoacid generators (PAG), and solvents. The matrix resin has a specific chemical structure. In the presence of acid, it will undergo a chemical reaction, causing a change in the solubility of the photoresist. During the exposure process of the photoacid generator PAG, it will absorb photons and then produce acid. This acid can act as a catalyst to trigger a polymer reaction. The solvent can adjust the viscosity and fluidity of the photoresist. In this way, a uniform film coating can be achieved. In traditional organic photoresists, the base resin changes its solubility through acid-catalyzed reactions. The photoacid generator PAG absorbs photons to produce acid, triggering polymer reactions. The solvent regulates viscosity and fluidity. With the help of the chemical amplification effect, traditional organic photoresists can achieve pattern transfer at low exposure doses. They have high sensitivity and excellent processing performance, which makes them of crucial significance in semiconductor manufacturing[7]. However, as the feature size of devices continues to shrink, traditional organic photoresists have encountered challenges in high-resolution applications. The movement and diffusion of polymer chains will increase the roughness of the pattern edges and also cause fluctuations in line width. This will have an impact on the quality and accuracy of the pattern. These movements may cause changes in edge roughness and line width, which limits their application in high-resolution lithography. In deep ultraviolet lithography technology, the resolution of traditional organic photoresists is approaching its physical limit and cannot meet the future demand for smaller feature sizes.

3.2. Novel Inorganic Photoresists

Novel inorganic photoresists are based on inorganic materials such as $Ge_2Sb_{1.5}Bi_{0.5}Te_5$ (GSbTe) and other phase-change materials with unique properties. GSbTe can reversibly change between amorphous and crystalline states. Through laser direct writing or thermal annealing, selected areas can transition from amorphous to crystalline. The significant difference in etching rates between the two states provides a basis for pattern formation. Experiments show that in KOH-H_2O_2 alkaline developer, the etching rate of polycrystalline GSbTe is approximately 1.6 Å/s, while that of amorphous GSbTe is about 0.72 Å/s[6]. This indicates that the polycrystalline state is more sensitive to alkaline solutions, making GSbTe suitable as a positive resist. Conversely, in HNO_3 - H_2O_2 - H_2O acidic developer, the etching rate of amorphous GSbTe is around 0.23 nm/s, and that of polycrystalline GSbTe is about 0.72 nm/s. This shows that the amorphous state is more sensitive to acidic solutions, making GSbTe suitable as a negative resist. This dual characteristic of positive and negative resists gives GSbTe photoresists high flexibility and adaptability for diverse semiconductor manufacturing needs. Fig. 1 (a) shows that in K-H alkaline solution, the etching depth of the GSBT film in both states has a roughly linear relationship with the development time, with a slope of 1.6 Å/s for the polycrystalline state and a slope of 0.72 Å/s for the amorphous state. It indicates that the polycrystalline state is more sensitive to the K-H alkaline solution compared to the amorphous state. Fig. 1 (b) shows the effect of N-H acid solution on the development characteristics of GSBT thin film photoresist.

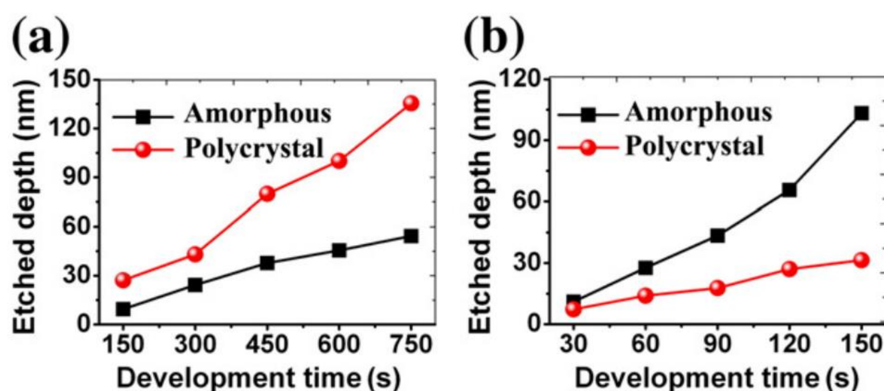

Fig. 1 The developing features of different phases of GSBT versus time. (a) In K–H alkaline solution. (b) In N–H acid solution [6]

4. Chemical Reaction Mechanisms in EUV Lithography

In EUV lithography, photoresists undergo complex photochemical reactions under 13.5nm high-energy radiation, including light absorption, photoionization, molecular dissociation, and ion/neutral fragment release. EUV photons have high energy (up to 92 eV), making the chemical reactions in EUV photoresists unique[6]. For example, experiments show that the absolute ion emission yield (AIOY) of PMMA (polymethyl methacrylate) is 8.8×10^{-4}, while that of amorphous and crystalline GSbTe reaches $2.25 \times 10^{-3}$and 9.7×10^{-4}, respectively. This highlights the varying reaction characteristics of different photoresists under EUV radiation.

4.1. Light Absorption and Photoionization

When the molecules or atoms in the extreme ultraviolet photoresist absorb photons, the phenomenon of photoionization occurs, generating free electrons and ions. The quantum yield of this process is generally close to 1 or greater than 1, which indicates that almost every absorbed photon will trigger an ionization event. High-energy free electrons can cause secondary reactions. Reactions like molecular dissociation and bond breaking can cause changes in the chemical structure and solubility of photoresist. Photoionization is the first step of the chemical reaction in EUV lithography, which has a crucial impact on the subsequent reaction process and the results obtained from lithography. To

study photoionization, we need to understand the reaction mechanism of EUV photoresist, so as to optimize its performance.

4.2. Molecular Dissociation and Fragment Release

High-energy electrons produced by photoionization interact with molecules in the photoresist, causing molecular dissociation and generating ions and neutral fragments such as H^+, F^+, $CxFy^+$, and $CnHm^+$. The release of F^+ is directly related to the fluorine content in the photoresist, while the release of hydrocarbon fragments (e.g., CH_3^+, $C_2H_5^+$) depends on the polymer type and structure of the photoresist. For example, photoresists containing specific functional groups (such as methacrylate or acrylate groups) release more hydrocarbon fragments under EUV radiation. In the case of PMMA, the main ions released are $CnHm^+$, while in fluorine-containing photoresists, F^+ release is more significant. These fragment releases not only affect the solubility and pattern formation of the photoresist but may also contaminate the optical systems of lithography equipment. Therefore, studying molecular dissociation and fragment release is crucial for optimizing EUV photoresist performance and enhancing the stability of lithography equipment.

4.3. Reaction Kinetics and Dill Parameters

By measuring the ion fragment intensity in EUV photoresists as a function of exposure dose, reaction kinetic parameters can be determined. Experimental data show that the ion intensity of released gases exhibits a natural logarithmic relationship with exposure dose, providing a basis for determining the reaction kinetics parameters of photoresists. The Dill parameter C describes the relationship between the consumption rate of reactants in the photoresist and the exposure dose. For the release of F^+ and CH_3^+ in EUV photoresists, the Dill parameter C can reflect the reactivity of different photoresist samples[2]. Photoresists with more fluorine content or specific polymer structures typically have higher Dill parameter C values, indicating faster reactions under EUV radiation. Determination of Dill parameters helps evaluate the reaction rate and sensitivity of photoresists, offering guidance for their optimal design.

5. Factors Influencing Chemical Reactions of EUV Photoresists

5.1. Photoresist Composition and Structure

The chemical composition and molecular structure of photoresist play a decisive role in its reaction characteristics in extreme ultraviolet lithography. If there are more aromatic structures in the photoresist, its stability will be higher, and fewer hydroxyl-containing fragments will be released. If there are more aliphatic structures in the photoresist, more carbon-hydrogen fragments will be released. Take this, for example. The more aromatic structures the photoresist has, the higher its stability will be and the fewer hydroxyl-containing fragments it will release. However, the more aliphatic structures the photoresist has, the more hydrocarbon fragments it will release. The types and contents of photoacid generators, namely PAGs, and other additives in the photoresist also have a significant influence on their photochemical reaction behavior. The type and content of PAG will directly affect the amount of acid generated in the photoresist and the reaction rate, which will influence the change in solubility and the formation of patterns. Other additives in the photoresist, such as alkaline additives and antioxidants, will also affect its performance. When considering all these factors need to be taken into account comprehensively.

5.2. Exposure Dose and Power

In EUV lithography, exposure dose and photon flux significantly influence the reaction rate and extent of photoresists. Higher exposure doses and power increase the probability of molecular ionization and dissociation in the photoresist, accelerating the reaction process. However, excessive exposure doses can lead to overreaction of the photoresist, causing pattern deformation or resolution reduction. For instance, the composition and structure of the photoresist determine its reaction

characteristics in EUV lithography. Photoresists with more aromatic structures have higher stability and release fewer hydroxyl-containing fragments, while those with more aliphatic structures release more hydrocarbon fragments. Exposure dose and power also have a significant impact on the reaction rate and extent of photoresists. Higher exposure doses and power increase the probability of molecular ionization and dissociation in the photoresist, thereby accelerating the reaction process[2]. However, excessive exposure doses can cause overreaction of the photoresist, leading to pattern deformation or resolution reduction. Therefore, precise control of exposure dose and power is essential for optimal lithography results. Optimizing exposure dose and power is crucial for improving lithography efficiency and pattern quality.

5.3. Photoresist Thickness

The thickness of the photoresist will affect its absorption of extreme ultraviolet light and the depth of the reaction. If the photoresist layer is relatively thick, it will increase the light absorption and scattering within the photoresist layer, which will affect the uniformity of the reaction and the accuracy of pattern transfer. Take the influence of photoresist thickness on the absorption and depth of the reaction of extreme ultraviolet light as an example. A thicker photoresist layer will increase the absorption and scattering of photons within the resist layer, affecting the uniformity of the reaction and the accuracy of pattern transfer. To achieve a better photolithography effect, precisely controlling the thickness of the photoresist is an indispensable condition. Generally, the thickness of the photoresist is controlled by adjusting the parameters of the rotary coating process. For example, the rotational speed, time, and the rate of solvent evaporation. Optimizing these parameters is crucial for obtaining uniform photoresist films and improving the quality of photolithography.

6. Chemical Reaction Mechanisms in DUV Lithography and Novel Aqueous-Based Bio-Photoresists

6.1. Characteristics of Aqueous-Based Bio-Photoresists

Water-based biological photo resizing agents are made from natural polysaccharides, and chitosan is one of them. This photo resizing agent is very environmentally friendly. Chitosan is extracted from the waste produced by the Marine industry. It has many advantages, such as being non-toxic, biodegradable, having the property of forming films, and being sensitive to ultraviolet rays etc. It is very suitable for use in deep ultraviolet lithography. Unlike traditional organic photoresisting agents, chitosan photoresizing agents use deionized water as the solvent and developer when in use. This avoids the use of organic solvents and alkaline developers, thereby reducing pollution to the surrounding environment and also lowering the risks that operators may face.

6.2. Chemical Reaction Mechanisms of Chitosan Photoresists

Using a 193 nm dry scanner for DUV exposure on a ~100 nm thick chitosan film. The irradiation dose of 600 to 900 mJ/cm² was applied to the chitosan film using a binary mask with multiple features, acting as a positive photoresist under chain-scission DUV irradiation. SEC investigation of 100 nm thick chitosan films showed that M significantly decreased after 600 mJ/cm² irradiation, with Đ dropping to 14 kg/mol and Đ being 2.02. Low molecular weight chitosan chains increase the solubility of the film and are removed during the development step in deionized water (pH ~ 6.5–7), while the unexposed areas remain undiluted and are preserved [7]. The binary patterns revealed after development show good imaging quality for patterns with a line/space (L/S) as low as 1 μm, as shown in Fig. 2. The optimal dose is 600 to 700 mJ/cm², higher than traditional photoresists (< 100 mJ/cm²). Before industrial implementation, it is necessary to enhance photosensitivity. Adding a photoacid generator (PAG) can improve the lithographic performance of chitosan-based photoresists [8, 9].

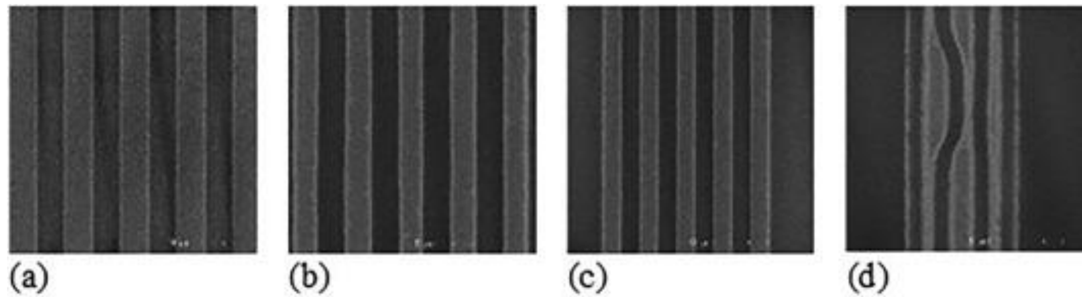

Fig. 2 Top-view CD-SEM images with chitosan dense trenches patterns. Half-pitch (HP) (a) HP 5 μm, (b) HP 2 μm, (c) HP 1 μm, (d) HP 0.7 μm after DUV exposures at 700 mJ/cm^2.[7]

6.3. Performance Optimization of Chitosan Photoresists

Currently, chitosan photoresists have relatively low sensitivity, with optimal exposure doses between 600-700 mJ/cm^2, higher than those of conventional organic photoresists (<100 mJ/cm^2) [7]. To improve sensitivity, photo acid generators (PAGs) can be added to chitosan photoresists. Under UV exposure, the acid generated by PAG promotes the dissolution of high molecular weight chitosan chains, enabling complete pattern formation at lower exposure doses. Additionally, chitosan photoresists need to improve sub-micron resolution. They exhibit issues such as incomplete pattern opening or deformation below 1 μm line/space (L/S) patterns, possibly due to surface tension during development. Further improvements are needed to enhance the contrast of chitosan photoresists.

7. Factors Influencing Chemical Reactions of DUV Photoresist

7.1. Photoresist Composition and Structure

The chemical structure and molecular weight of chitosan significantly affect its lithographic performance. Parameters such as the degree of acetylation (DA), molecular weight (Mw), and dispersity (Đ) of chitosan influence its solubility, film-forming properties, and photochemical reactivity. For example, chitosan with a DA of 35%, Mw of 693 kDa, and Đ of 1.8 exhibits good performance in DUV lithography. The types and content of PAGs added to chitosan photoresists also significantly impact their reactivity and pattern formation capabilities [10].

7.2. Exposure Dose and Power

Exposure dose is a key factor affecting the pattern formation of chitosan photoresists. Higher exposure doses increase the degree of chitosan molecular chain scission, enhancing solubility. However, excessive exposure doses can cause pattern deformation or resolution reduction. Therefore, precise control of exposure dose is necessary for optimal lithography results.

7.3. Photoresist Thickness

Photoresist thickness also significantly impacts DUV lithography outcomes. Thicker photoresist layers increase light absorption and scattering within the resist layer, affecting reaction uniformity and pattern transfer accuracy. Therefore, precise control of photoresist thickness is necessary, typically achieved by optimizing spin-coating process parameters [11].

8. Challenges, Optimization Directions, and Progress in Lithography and Photoresist Materials

8.1. Challenges in Lithography Technology Development

Despite the theoretical basis for higher resolution provided by shorter wavelengths in lithography technology evolution, numerous challenges arise in practical applications. For example, in extreme ultraviolet (EUV) lithography, insufficient light source power is a critical issue. Literature reports

that current EUV light source power is only 10% of that of traditional deep ultraviolet (DUV) light sources, significantly prolonging exposure time and reducing lithography production efficiency[12]. To meet high-volume production demands, exposure doses must be optimized to balance pattern quality and production efficiency.

Optical system design also significantly impacts EUV lithography outcomes. Due to the extremely short wavelength of EUV lithography, the reflectors and lenses in the optical system must have extremely high precision and surface quality. Studies show that for every 0.1 increase in the numerical aperture (NA) of an optical system, resolution can improve by approximately 10%. However, increasing NA imposes stricter requirements on optical element manufacturing. For instance, when NA reaches 0.55, the surface roughness of optical elements must be controlled within 0.3 Å; otherwise, optical imaging quality will decline, affecting the accuracy of lithography patterns[1].

Additionally, the chemical reaction characteristics of photoresists under EUV radiation are crucial for lithography outcomes. Traditional organic photoresists in EUV lithography suffer from molecular chain movement and diffusion, leading to increased pattern edge roughness and line width fluctuations. For example, experiments show that traditional organic photoresists under 13.5 nm EUV radiation exhibit pattern edge roughness of up to 2.5 nm and line width fluctuations of 3%-5%, limiting their application in high-resolution lithography[8]. Therefore, developing novel photoresist materials to meet EUV lithography demands is urgently needed.

8.2. Optimization Directions for Photoresist Materials

In optimizing photoresist materials, reducing the Rayleigh constant is key to improving resolution. By improving photoresist formulations, the Rayleigh constant can be lowered to enhance lithography resolution. For instance, $Ge_2Sb_{1.5}Bi_{0.5}Te_5$ (GSbTe) materials, with their reversible phase change between amorphous and crystalline states, offer new ideas for photoresist optimization. Experiments show that in KOH - H_2O_2 alkaline developer, the etching rate of polycrystalline GSbTe is approximately 1.6 Å/s, while that of amorphous GSbTe is about 0.72 Å/s. In HNO_3 - H_2O_2 - H_2O acidic developer, the etching rate of amorphous GSbTe is around 0.23 nm/s, and that of polycrystalline GSbTe is about 0.72 nm/s. This dual positive and negative resist characteristic gives GSbTe photoresists high flexibility and adaptability for different types of pattern manufacturing, meeting diverse semiconductor manufacturing needs[3].

Furthermore, improving the sensitivity of photoresists is another optimization direction. Traditional organic photoresists struggle to achieve complete pattern transfer at low exposure doses. However, adding photo acid generators (PAGs) can enhance sensitivity. For example, adding an appropriate amount of PAG to photoresists can reduce exposure doses to 60%-70% of the original value. Additionally, photoresist thickness control is crucial for EUV lithography outcomes. Thicker photoresist layers increase photon absorption and scattering within the resist layer, affecting reaction uniformity and pattern transfer accuracy. Experiments show that a 10% increase in photoresist thickness can increase pattern edge roughness by 1.2 nm and expand line width fluctuations by 1%-2%.[2] Therefore, precise control of photoresist thickness is vital for improving lithography quality.

8.3. Optimization Directions for Photoresist Materials

In optimizing photoresist materials, experimental validation is key. For instance, experiments show that the absolute ion emission yield (AIOY) of PMMA (polymethyl methacrylate) is 8.8×10^{-4}, while that of amorphous and crystalline GSbTe reaches 2.25×10^{-3} and 9.7×10^{-4}, respectively. This highlights the varying reaction characteristics of different photoresists under EUV radiation. By measuring the ion fragment intensity in EUV photoresists as a function of exposure dose, reaction kinetic parameters can be determined. Experimental data indicate a natural logarithmic relationship between the ion intensity of released gases and exposure dose, providing a basis for determining photoresist reaction kinetics parameters. The Dill parameter C describes the relationship between the consumption rate of reactants in the photoresist and exposure dose. For the release of F^+ and CH_3^+ in

EUV photoresists, the Dill parameter C reflects the reactivity of different photoresist samples. Photoresists with more fluorine content or specific polymer structures typically have higher Dill parameter C values, indicating faster reactions under EUV radiation. Determination of Dill parameters helps assess the reaction rate and sensitivity of photoresists, offering guidance for their optimal design[2].

In practical applications, photoresist thickness adjustment can be achieved by optimizing spin-coating process parameters such as spin speed, time, and solvent evaporation rate. Experiments show that increasing spin speed by 500 rpm reduces photoresist thickness by approximately 10%. Precise control of spin-coating parameters yields uniform photoresist films, enhancing lithography quality. The composition and structure of photoresists also critically influence their reaction characteristics in EUV lithography. Photoresists with more aromatic structures exhibit higher stability and release fewer hydroxyl-containing fragments, while those with more aliphatic structures release more hydrocarbon fragments. The types and content of photo acid generators (PAGs) and other additives significantly affect photoresist photochemical reactions. PAG types and content directly impact acid generation and reaction rates, thereby influencing solubility changes and pattern formation. Additionally, other additives in photoresists, such as basic additives and antioxidants, also impact performance and need to be considered comprehensively[12].

9. Summary

Lithography technology, as a core process in semiconductor manufacturing, reflects the microelectronics industry's pursuit of higher performance and smaller sizes. From ultraviolet to deep ultraviolet and now to extreme ultraviolet lithography, each technological iteration has significantly enhanced lithography resolution, meeting the demands of device miniaturization. However, as device feature sizes approach physical limits, lithography technology faces unprecedented challenges.

In terms of photoresist material optimization, conventional organic photoresists are limited by molecular chain movement and diffusion in high-resolution lithography and fail to meet future demands for smaller feature sizes. In contrast, novel inorganic photoresists such as $Ge_2Sb_{1.5}Bi_{0.5}Te_5$ (GSbTe) offer significant potential with their unique dual positive and negative resist characteristics and reversible phase change between amorphous and crystalline states. The etching rate differences of these materials in different developers provide new possibilities for pattern formation and new ideas for photoresist optimization.

Through in-depth studies on the chemical reaction mechanisms of photoresists in EUV and DUV lithography, it has been found that processes such as light absorption, photoionization, molecular dissociation, and fragment release are key factors affecting lithography outcomes. In EUV lithography, the absorption of high-energy photons by photoresists and the free electrons and ions generated by photoionization trigger a series of complex chemical reactions, altering the solubility and pattern formation characteristics of the photoresist. In DUV lithography, the emergence of novel environmentally friendly photoresists such as chitosan not only reduces environmental impact but also provides a new direction for sustainable photoresist material development.

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