

“Materials and Production” field

Achievement : Development of chemically amplified resist polymer materials for innovative semiconductor manufacturing process

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Summary

The most important key technology which has been the driving force for innovation in semiconductor technology over the past half a century is lithography, which engraves fine circuits in semiconductors. Dr. Grant Willson and Dr. Jean Fréchet, along with the late Dr. Hiroshi Itoh, embarked on the development of the resist to be used for lithography in the early 1980's, and succeeded in developing a new key technology known as a chemically amplified resist. Through the use of resist developed jointly by the three doctors, a lithography using a short wavelength deep ultraviolet (deep UV; wavelength 254nm) was achieved. By improving this chemically amplified resist, an era of the next generation integrated circuit with a minimum semiconductor circuit width of under 250nm was opened up. The chemically amplified resist is an important technology for the extreme ultraviolet lithography (EUV; wavelength 1-10nm), a present leading edge technology, as well as for electron lithography, and is a key technology in creating new types of electronics.

Advancements in photolithography has supported the development of semiconductor integrated circuits

Progress in semiconductor integrated circuits (IC) which were developed in the 1960's has been made by improvements in the device density. According to “Moore's Law” which has become well-known as a result of the paper published in 1965 by Gordon Moore, a co-founder of Intel Corporation, it was estimated that “the number of transistors of integrated circuits will double every 24 months.” This has become a reality, giving birth to an advanced information society.

The greatest contribution made to the advancement of integrated circuits is this most important key technology called lithography, which is a microfabrication technology. “Litho” means stone, and “graphy” means to write; thus, it can be said that semiconductor lithography is a technology in which fine electronic circuits are written on silicon wafers.

Diagram 1 shows the lithography process in the manufacture of semiconductors. First of all, a polymer film called resist is applied to the silicon wafer to be processed through spin coating. A photo-

chemical reaction occurs within the resist when exposed to light. There are two types of resist materials, one being easy to dissolve in a solvent called the developer and the other is not.

Thus, when the resist is exposed and developed through a photo-mask in which a circuit pattern is written, a resist pattern corresponding to the mask pattern is written. Furthermore, the process using chemicals or plasma to process the area not covered by the resist is called etching. Last of all, after the resist is removed through polishing, a silicon wafer configured to the desired design is attained. There are positive type and negative type resists; the positive type is the one in which the exposed area dissolves in the developer, and the negative type is the one in which the exposed area remains.

The properties of the resist play an extremely important part in increasing the device density of the integrated circuit. In the early days, known polymers with photochemical reactions were used on the resist. However, gradually new types of resist materials have been pursued with higher exposure sensitivity, higher resolution in order to write finer circuits, and with superior etching resistance.

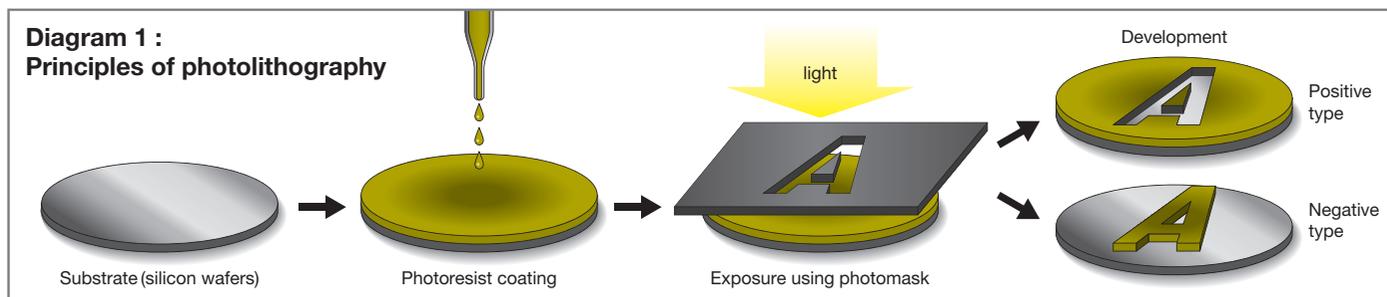
Catalysts formed through chemical reactions create a chain reaction

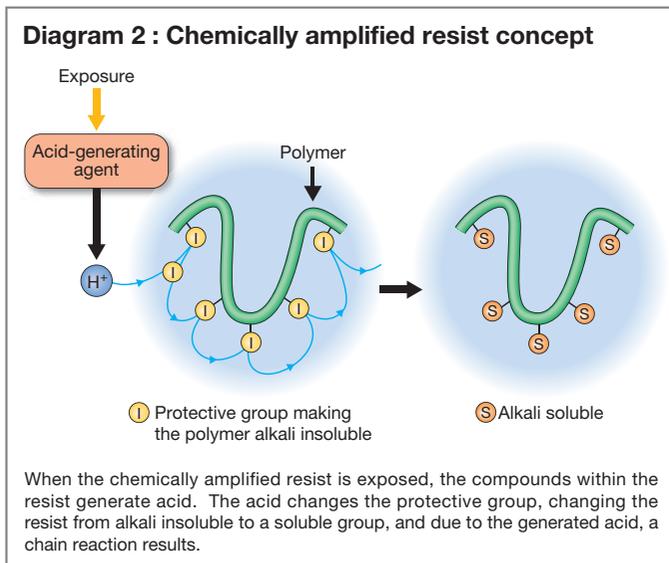
In the latter 1970's at the IBM Research Laboratory located in San Jose, a central Silicon Valley city in California, U.S.A., the development of new resist materials was underway. At that time, Dr. Grant Willson was the head of the resist development.

One way to improve the resolution of the semiconductor lithography is to shorten the wavelength of the ultraviolet rays used for resist exposure. However, when the wavelength was shortened, a problem arose in that the resist exposure sensitivity was significantly reduced, making it difficult to write a circuit. Lithography using light was approaching its limit, so an electron lithography was proposed. Due to cost problems, however, efforts were made to stretch the potential of the conventional lithography to the limit.

At the time, Dr. Willson's goal was the resist development to attain a lithography using the deep UV of a conventional high-pressure mercury lamp with the shortest wavelength of 254nm. In order to achieve that goal, in 1979, Dr. Jean Fréchet, an associate professor at the University of Ottawa in Canada who was engaged in the function study of polymers, made use of the sabbatical system (a long-term paid leave given to a university teacher over a certain period of time in order for him to dedicate himself to research) and joined in the development. Thereafter, he became a partner in resist development. In the following year, the late Dr. Hiroshi Itoh (~2009), who was studying polysaccharide synthesis at the State University of New York, came to work under Dr. Willson as a postdoctoral fellow.

The research team headed by Dr. Willson, Dr. Fréchet and the late Dr. Itoh paid particular attention to chemically amplified resist as a method to improve the resist sensitivity. With chemically amplified resist, a catalyst known as the active species is first created within the resist through light exposure. It was thought that by merely causing the catalyst to create a chain of chemical reactions within the resist, the polymer properties of the resist can be changed at once by a slightest exposure to light. Among the researchers were some who pointed





out that due to unregulated chain reactions that occur in chemically amplified resist, the resolution may conversely deteriorate even if the exposure sensitivity improves. However, they decided to undertake the challenge.

While repeating the trial and error process, in 1980, the research team succeeded in developing a resist material which creates an extremely stable reaction during resist synthesis even under light exposure. According to the paper published in 1982, a chemically amplified resist was proposed (diagram 2) in which acid is generated as active species, and the resultant acid successively changes the protective groups which protect the polymers from the alkali solvent used in exposure. Such a resist was actually synthesized, and the first chemically amplified resist used for semiconductor manufacture was a polymer in which t-butoxycarbonyl (tBOC) was removed with acid, producing polyhydroxystyrene (PHS) (deprotection reaction).

A chemically amplified resist overcame obstacles the semiconductor technology was facing

The resist developed at this time became the prototype for the later positive-type resist, and various chemically amplified resists were subsequently developed. At IBM, a chemically amplified resist was used in a 1 megabit DRAM production with a minimum integrated circuit width of $1\mu\text{m}$. However, in general, it came to be widely used in what was called the next generation DRAM in lithography with a minimum width of 250nm. Dr. Willson, Dr. Fréchet and the late Dr. Itoh continued their joint research thereafter on chemically amplified resists, and contributed to the development of semiconductor lithography. Dr. Willson and Dr. Fréchet have expanded their research field to include studies on various polymer functions.

Chemically amplified resists have proved useful in lithography using the KrF excimer laser with a wavelength of 248nm, which plays a key role in the present semiconductor exposure device. Additionally, chemically amplified resists are playing an important part in extreme ultraviolet (EUV) lithography and electron lithography which are receiving widespread attention as the next generation semiconductor technology, and continue to serve as key technology in paving the way for new electronics technology to this day.

What became the driving force to overcome the limitations of the semiconductor lithography in the 1970's was the chemically amplified resist developed by three scientists. Through the emergence of the chemically amplified resist, it can be said that the electronics industry has been able to follow the development as predicted by "Moore's Law."