Polyimides in Microelectronics Applications

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Applications for polyimides in microelectronics were reviewed. Only materials that can retain sufficient reliability for severe heat conditions (180-400°C) can be used as insulation materials for electronics. Polyimides are an invaluable organic materials that satisfy the heat resistance requirement. For polyimides, fine patterning technologies of below 1 micron have been established. These technologies are sufficient for wiring board applications and passable for LSI wiring. Dielectrics with low k become necessary for high performance electronic products Table 1 lists k for various inorganic materials and organic polymers. Except for Teflon and polyethylene, polyimides give the lowest k. A large number of monomers with a variety of structures offer wide possibilities for molecular design of polyimides. Now-a-days, corresponding to strong demands for better electrical consumer products, many kinds of applications are spreading widely; e.g. LSI buffer coat films, TAB tapes, adhesives for LSI packaging, liquid crystal orientation films, and optical application fields such as waveguides. Polyimides will be more important material in electronics, because of their superior properties coupled with wide design tolerance.

Keywords: polyimide, microelectronics, heat resistance, dielectric constant

1. Polyimide features
1.1 Heat resistance

Electronics related manufacturing involves many high temperature steps: starting from the LSI production to its' when mounted on a board. The materials making up the devices and the packaging materials must be able to survive the thermal stress of these high temperature processes.

As an example, from LSI manufacturing and packaging, the technique that makes the connection between elements electrically and/or optically to give a specific function to the elements, is explained. First, in the LSI wiring process, a heat treatment at about 400°C for 1 h is applied for deposition of wiring metal and its' annealing. Because this is repeated for each wiring layer, the interlayer dielectrics for the first level wiring undergo this high temperature process several times. Heat stability is essential for the interlayer dielectrics, because evolution of decomposition gas from the materials during the wiring process causes a fatal decrease in the quality of the wiring metal.

Fabricated LSI chips next are packaged process and molded into LSI packages (LSI packaging). After making electrical connections (wire bonding, solder ball, etc.) to connect the LSI and the outside, it is molded in an epoxy resin, etc. The LSI packaging process usually involves temperatures of 180°C or higher temperature, depending on the kind of package. In addition, when mounting these LSI packages on the wiring board (computer packaging), the packages are heated to about 250°C for a moment by IR irradiation.

Only materials that can retain sufficient reliability for these severe heat conditions can be used as insulation materials for electronics. Polyimides are an invaluable organic materials that satisfy the heat resistance requirement.

1.2 Fine patterning

LSI wiring is getting finer for each new generation. The wiring rule for 64M DRAMs is 0.3 -0.2 microns, and in next decade the rule might go down to 0.1 micron. Feasibility of this fine patterning depends strongly on LSI interlayer dielectrics.

The need for fine patterning of wiring boards is strong too, for efficient high density packaging.
Conventionally, wiring rules of wiring boards have been larger than 100-micron lines and spaces (L/S). But in now-a-days, in some consumer products such as handy phones, handy cams, etc., wiring boards with below 100-micron L/S wiring are used. And in some specific applications, wiring boards with 10-micron L/S wiring are required.

For polyimides, fine patterning technologies of below 1 micron have been established. These technologies are sufficient for wiring board applications and passable for LSI wiring.

### 1.3 Low dielectric property

For high performance electronic products, an improvement of the operation frequency of the LSI and high-speed transmission of electric signals in the wiring board become essential. These properties can be described as functions of the dielectric constant \( k \) of the dielectrics; operating frequency is inversely proportional to the \( k \) of the dielectrics; transmission velocity is inversely proportional to the \( 1/2 \) power of the \( k \) of the dielectrics. Therefore, dielectrics with low \( k \) become necessary.

Table 1 lists \( k \) for various inorganic materials and organic polymers. Except for Teflon and polyethylene, polyimides give the lowest \( k \).

### 1.4 Design tolerance

The properties, heat resistance, fine patterning, and low \( k \) etc., just described can be realized even for materials such as specific poly benzoxazole, and polyquinoline, and fluorinated polyaryl ether. Since the synthesis of polyimides by Sroog at Du Pont and others, researchers and engineers have developed many monomers and synthesis methods. For applications in the electronics field, various properties are required depending on places and conditions.

A large number of monomers with a variety of structures offer wide possibilities for molecular design of polyimides.

### 2. Polyimides as LSI interlayer dielectrics

Synthesizing the most suitable LSI interlayer dielectrics is a difficult target, but the polyimides will give a large impact in electronics. Besides the heat resistance, thermal expansion coefficient (TEC) and dielectric constant \( k \) are most important properties.

#### 2.1 Low thermal expansion coefficient (TEC)

As mentioned above, the LSI production process includes high temperature processes, and a large heat stress between different kinds of materials may cause crucial problems. Low thermal expansion polyimides having TECs ranging from 1 ppm/K (close to the value of Si) to 20 ppm/K (close to the value of Al and Cu) had far reaching effects, because polyimides could solve the problem caused by thermal stress. Possible applications to the electronics field are wide spread. Polyimides with linear structure give low TEC. PI(BPDA/p-PDA) is
the most widely used low TEC polyimide. High reliability of multilayer wiring LSIs with polyimide dielectrics has been reported.

TEC of a polyimide depends on not only its chemical structure, but also the imidization process. Relationship between imidization process and TEC of the polyimide is important for industrial use, and some results have been reported. Figure 1 shows the amount of residual NMP in the PAA film after drying and the TEC of fully imidized polyimide films. Film thickness, drying temperature, and drying time ranged from 5 to 20 mm, 80 to 120°C and 0.5 to 3 h, respectively. Formation of thermally stable molecular compounds between polyamic acid unit and 2 NMP molecules (1/2 compound) has been reported. TEC was a minimum when PAA film contained about 33% residual NMP, corresponding to quantitative formation of the 1/2 compound, and this was independent of film thickness and drying conditions. These results proved clearly that TEC of the polyimide film is controlled by formation of the 1/2 compound during the drying process.

2.2 Low k property

Higher operation frequency is indispensable for performance improvement of LSIs. Frequency (F) that wiring can transmit is represented by \( F \propto \frac{1}{(\rho \cdot k)} \), and it is inversely proportional to specific resistance (\( \rho \)) of the wiring and the dielectric constant (\( k \)) of the dielectrics. Therefore, using of low \( k \) dielectrics is inevitable for high performance LSIs. It is certain that performance of Al wiring and SiO insulation film (\( k=4.0 \)) system will hit a ceiling in the near future and many investigations of wiring metal and dielectrics are being made now. Cu is the only metal which can be used practically as a low \( \rho \) wiring. SiO-F(\( k=3.4 \cdot ) \), low \( k \) SOG, and organic polymer materials including fluorinated polyimides are candidates for low \( k \) dielectrics for LSIs.

Introduction of fluorine atoms is effective for reducing \( k \) of dielectrics. Fig. 2 illustrates the relationship between the polyimide, TEC and dielectric constant. Fluorine containing polyimides with a linear structure exhibit low \( k \) and low TEC. Lower limit of \( k \) attained by bulk polyimide might be higher than 2.4. To achieve a much lower \( k \) beyond this, nano porous polyimides have been studied by IBM researchers.

3. Photosensitizing

LSI buffer coat film is one important application of polyimides. Fig. 3 shows a trends in LSI buffer coat film formation process. The photo sensitive polyimide (PPI) process has a large merit being short and it is replacing the conventional non-photosensitive PI process. To date, many negative type PPIs developable in organic solvent have been developed and applied to some LSIs.
In the future, an alkali water solution developable positive type PPI which is superior in safety and productivity, that can be used in the same process as the present positive type resist will replace conventional PIs and negative type PPIs. In the past several years, positive type PPIs have been announced from Shinnestu Chemical, Nissan Chemical, Hitachi Chemical, etc.

4. Scope

Research on polyimides in the electronics field until the 80's was put towards large-sized computers. Now-a-days, corresponding to strong demands for better electrical consumer products, many kinds of applications are spreading widely; e.g. LSI buffer coat films, TAB tapes, adhesives for LSI packaging, liquid crystal orientation films, and optical application fields such as waveguides. Polyimides will be more important material in electronics, because of their superior properties coupled with wide design tolerance.

5. References