● Novel inorganic ion catcher “ IXE®-700H ”

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1. Introduction

In recent years, copper wire has been commonly used as a wiring material in semiconductor packages because of its many favorable properties, including high electrical conductivity and thermal conductivity. However, it oxidizes more easily than the traditionally used gold, and is known to be prone to copper electrochemical migration when combined with encapsulants. Copper migration is a phenomenon in which copper ions (Cu^{2+}) are eluted by electrical or chemical factors, migrate between electrodes or wires, and deposit as metallic copper on the opposing electrode or wiring. This phenomenon causes electrical short circuits and circuit failures, which adversely affect the reliability and service life of semiconductors. Therefore, countermeasures are required.

There are various causes of copper migration. One major cause is ionic impurities in the encapsulant, especially chloride ions (Cl^-). Cl^- is involved in a series of repeating redox reactions, as shown below, and acts as a factor that induces copper migration [1, 2].

$$\begin{array}{llll} (\text{Anode}) & Cu + 2Cl^{-} & \rightarrow & CuCl^{2} + 2e^{-} \\ & CuCl_{2} & \rightarrow & Cu^{2+} + 2Cl^{-} \\ (\text{Cathode}) & Cu^{2+} + 2e & \rightarrow & Cu \end{array}$$

There are two main approaches to suppressing copper migration. The first approach is to reduce the quantity of Cl^- in the encapsulant. The epoxy resins used in encapsulants contain chlorine atoms derived from the raw materials used in their manufacturing process. For this reason, Cl^- is known to be released by hydrolysis, and research into halogen-free synthesis methods and high-efficiency production technologies is underway. However, since encapsulants are composed of not only epoxy compounds but also multiple raw materials, such as curing agents, fillers, and various additives, they are likely to be contaminated by ionic impurities, making complete prevention difficult.

The second approach is adding an inorganic ion exchanger. Scavenging ionic impurities in the encapsulant can inhibit copper migration caused by ions.

2. Inorganic anion exchanger

Table 1 shows the scavenging performance of our inorganic anion exchangers for representative grades.

Table 1: Performance of inorganic anion exchangers

	Inorganic anion exchanger	Main component	Total ion exchange capacity (meq/g)	Exchange capacity of ions in the neutral pH range (meq/g)
Our product	IXE-550	Bi-based	3.7	1.8
	IXE-700F	Mg, Al-based	4.5	1.4
Comparison example	Activated alumina	Al	0.6	< 0.1
	Hydrated titanium oxide	Ti	0.5	< 0.1
	Cerium hydroxide	Ce	0.6	< 0.1

Total ion exchange capacity: Cl^- ion exchange capacity in 0.1 N-HCl
Exchange capacity of ions in the neutral pH range: Cl^- ion exchange capacity in 0.1N-NaCl

In addition to its high ion exchange performance, our inorganic ion exchanger IXE® consists of fine particles ranging in size from 0.2 µm to several µm and is used to improve the reliability of electronic materials, such as semiconductor packages [3].

The ion exchange capacity of typical ion exchange resins is approximately 1 meq/g, and for inorganic anion exchangers as well, 1 meq/g serves as the practical performance benchmark. As shown in **Table 1**, our inorganic anion exchangers exhibit a high total ion exchange capacity. Even in the neutral pH range, they show higher ion exchange performance than that of typical inorganic anion exchangers, such as activated alumina and hydrous titanium oxide.

Since pH is an important factor in maintaining the reliability of semiconductor packages [4], in general, the encapsulant resin (or more precisely, the resin extraction solution) should be in the neutral pH range. For this reason, it is necessary to discuss not only the total ion exchange capacity but also the capacity in the neutral pH range.

3. New inorganic anion exchanger, IXE-700H

In the field of electronic materials in recent years, semiconductor device miniaturization has driven narrower wiring pitches, and highly durable materials are being developed for power semiconductor applications. As a result, requirements for ion exchangers have become more stringent year by year. To meet these next-generation needs, we have developed IXE-700H, a new inorganic anion exchanger with even higher performance.

IXE-700H is composed of inorganic components that are not designated as RoHS restricted substances and has high heat resistance. Among existing IXE grades, it offers the highest anion adsorption performance in the neutral pH range.

3.1 Physical property values

Table 2 lists the typical physical properties of IXE-700H.

Table 2: Physical properties of IXE-700H

Item	Physical properties
Appearance	White powder
Main component	Mg, Al-based
Median diameter	Up to 1.0 μm
Heat resistance temperature	Up to 600°C
Aerated bulk specific gravity	Approx. 0.26 g/ml

3.2 Ion exchange performance test in water

Ion capture tests were conducted in water to evaluate ion exchange performance simply and quickly. The detailed test methods are described below. A 50 mL of aqueous chloride solution with a Cl^- concentration of 0.1 M and adjusted pH levels of 1, 3, 5, and 8, respectively, was prepared. Then, 1 g of IXE was added, shaken, and stirred for 20 hours to bring the ions in the solution into contact with IXE. Then, IXE was removed through a membrane filter, and the filtrate was diluted 1,000-fold to measure the Cl^- concentration by ion chromatography.

Based on the Cl^- concentration before and after the test, the ion exchange capacity (meq/g) was calculated using Equation 1. Ion exchange capacity refers to the quantity of ions scavenged per unit weight of the sample, which is usually expressed in milliequivalents per gram of sample (meq/g).

(Equation 1)

$$\text{Ion exchange capacity (meq/g)} = \frac{(A-B)\times E\times C}{D\times 1000\times S}\times F$$

A : Cl^- concentration before the ion exchange performance test (μg/ml)
B : Cl^- concentration after the ion exchange performance test (μg/ml)
C : Total volume of the test solution (ml)
D : Atomic weight of measured ion species
E : Dilution ratio of the test solution
F : Valence of the measured ion species
S : Amount of reagent (g)

Figure 1 shows the test results for our anion exchangers, IXE-700F and IXE-700H. IXE-700H exhibited an ion exchange capacity of nearly 3 meq/g across a broad pH range of pH 3 to 8, demonstrating its superior ion exchange performance, which is approximately twice that of IXE-700F over a wide pH range.

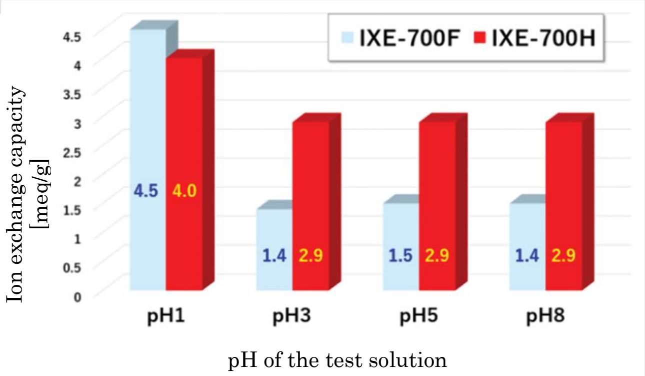


Figure 1: Ion exchange performance of IXE-700H in water

3.3 Ion exchange performance test using encapsulant resin

Epoxy materials used for semiconductor encapsulants are generally weakly acidic to neutral. For this reason, it is necessary to efficiently scavenge impurity ions in the near-neutral pH range. To evaluate whether IXE-700H exhibits ion exchange performance even in encapsulant resins, two types of experiments were conducted: an ion exchange performance test using an extracted solution from an encapsulant resin and a hot water extraction test with IXE kneaded into an encapsulant resin.

3.3.1 Preparation of epoxy curing resin

Cresol novolac epoxy resin (13 parts), novolac phenolic resin (16 parts), fused silica (70.9 parts), and phosphorus curing accelerator (0.1 parts) were mixed and kneaded in a Labo Plastomill. In the hot water extraction test, ion exchanger IXE (0.5 parts) was added to the above mixture and kneaded. Then, the kneaded material was thermally cured by heating at 150°C for two hours and 180°C for six hours. The resulting cured material was crushed and sieved through a 150 μm-sieve to prepare test pieces. In addition, the tensile test results confirmed that the glass transition temperature (Tg) of this cured epoxy resin is above 160°C. Then, the temperature condition for the hot water extraction test was set at 125°C.

3.3.2 Ion exchange performance test using resin extract

To prepare 30 mL of cured epoxy resin extract, 1 g of crushed cured epoxy resin after sieving without IXE, and 30 mL of ultrapure water were placed in a Teflon container, which was then tightly sealed and heated at 125 °C for 24 hours. The pH of the extract was 6.8, and the Cl^- concentration was 78 ppm. Then, 5 mg of IXE-700F and IXE-700H were added, respectively. After shaking and stirring for 20 hours, IXE was filtered out to measure the concentration of Cl^- in the filtrate. The results of the ion exchange capacity calculation in

Equation 1 showed that IXE-700H exhibited high ion exchange performance, even for the test solution in the neutral pH range of 6.8 (**Figure 2**).

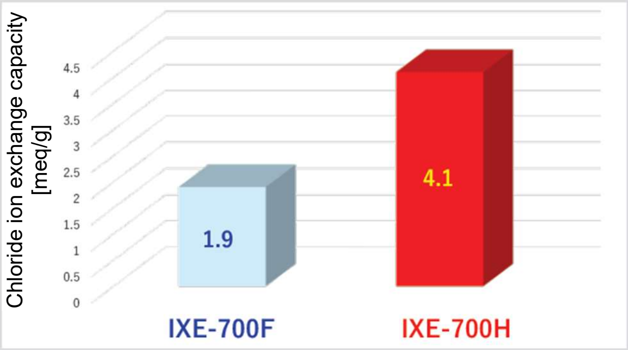


Figure 2: Ion exchange performance of IXE-700H in resin extract

3.3.3 Hot water extraction test

Next, 1 g of crushed cured epoxy resin that had been kneaded with 0.5 wt% of IXE, and 30 mL of ultrapure water were placed in a Teflon container, which was then tightly closed and subjected to hot water extraction treatment at 125°C for 24 hours. The Cl$^-$ concentration of the hot water extracts in the cured resin with and without adding IXE was measured to calculate the reduction rate of the Cl$^-$ concentration by adding IXE. IXE-700H exhibited high Cl$^-$ exchange performance, even when kneaded into resin (**Table 3**).

Table 3: Cl$^-$ concentration in hot water extracts

Sample name	Cl$^-$ concentration reduction rate
Extract of IXE-700F-kneaded cured resin	86%
Extract of IXE-700H-kneaded cured resin	94%

3.4 Reliability test under high temperature and humidity (HAST)

The cured epoxy material to which 1 wt% of IXE-700H had been kneaded was coated onto the comb-shaped copper wiring for FPCs (line spacing = 50 μm/50 μm) at a thickness of approximately 300 μm. The High Accelerated Stress Test (HAST) was conducted using the coated copper wiring at 130°C and 85%RH, with an applied voltage of 45 V for 500 hours, to observe changes in the resistance. When a short circuit occurs in the copper wiring, the resistance drops significantly. A decreased resistance condition was considered defective. The time until defects occurred was compared with and without adding IXE to the cured epoxy material in order to evaluate the reliability of moisture resistance of the copper wiring.

The resistance and voltage changes of the copper wiring are shown in **Figure 3**. **Figure 4** shows a photo of the copper wiring after 40 hours. Adding 0.5 wt% of IXE-700H significantly increased the time until the initial defect of copper wiring occurred, extending it from 34 hours without IXE to 194 hours and suppressing copper wiring short circuits. This indicates that adding IXE-700H significantly improves the moisture resistance reliability of copper wiring.

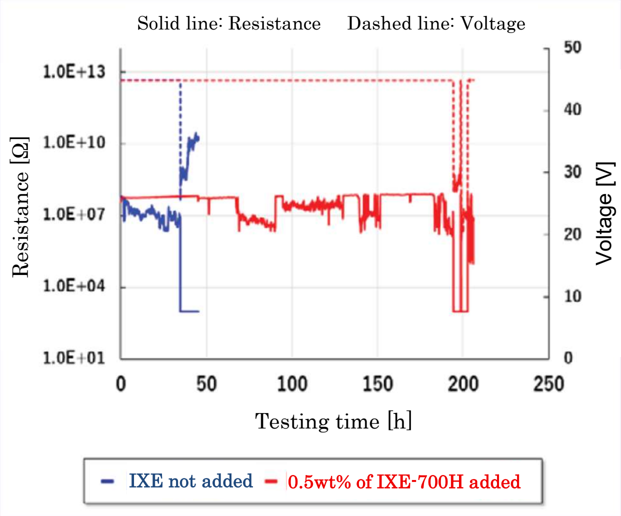
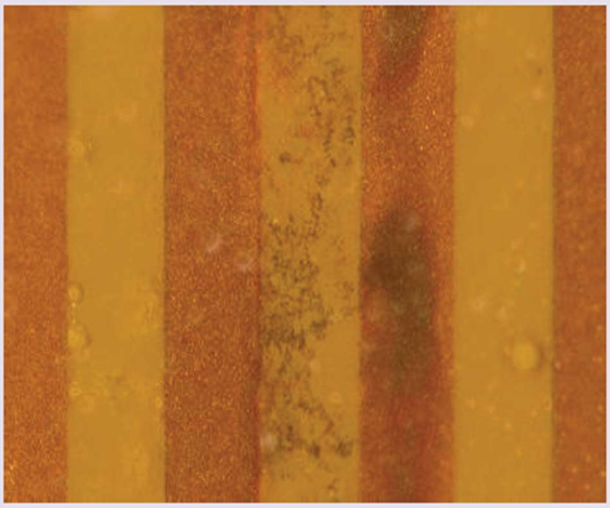
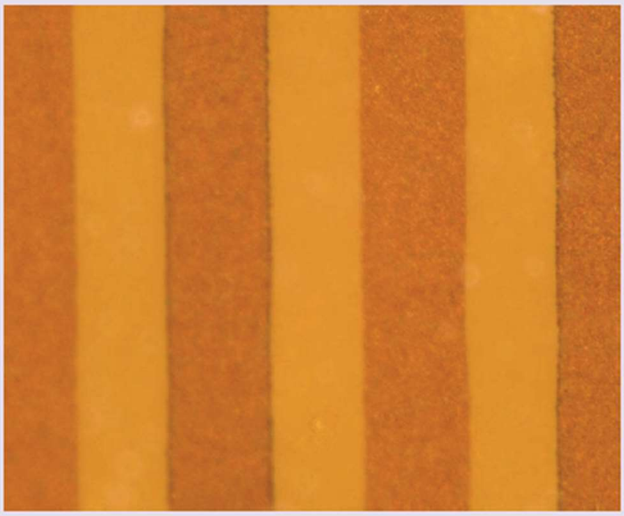


Figure 3: Wiring resistance and voltage change



IXE not added



0.5wt% of IXE-700H added

Figure 4: Photo of copper wiring after 40 hours

4. Conclusion

Technology in the semiconductor sector has made remarkable progress, leading to technical innovation at a rapid pace. In line with this, the development of materials for next-generation semiconductors, such as those for 5G technology and electric vehicles, has been pursued proactively. We will continue to focus on research and development to meet emerging needs and also strive to develop ion exchangers that can satisfy various demands.

Reference

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