Development of Functional Electronic Materials at KOBELCO

Yuki TAUCHI[*1] · Dr. Mototaka OCHI[*1] · Dr. Toshihiro KUGIMIYA[*2]

[*1] Applied Physics Research Laboratory, Technical Development Group
[*2] Planning & Administration Department, Technical Development Group

Abstract

To enhance the performance of expanding electronic devices, maximizing the functionality of electronic materials is crucial. Hence, when developing these materials, it is essential to consider the device manufacturing process and device structure. Kobe Steel has thus been simultaneously advancing the construction of manufacturing processes and device evaluation technology. In the development of oxide semiconductor materials, Kobe Steel has not only conducted electronic evaluations of individual materials, but has also proceeded with the creation and evaluation of thin-film transistors, revealing the correlation between device characteristics and material properties. Furthermore, in the development of recording films for optical disks, Kobe Steel has conducted recorded signal evaluations in conjunction with materials development. This paper explains the essential technologies for developing electronic materials that customers and users can confidently rely on.

Introduction

Technological advances involving digital devices, AI, and the shift to electric vehicles are all elements of our electronics-driven society. Alongside these advances, the parameters required of electronics are constantly evolving. The technologies that support electronic materials are indispensable for meeting such parameters, as these materials ensure the maximum functionality of electronic devices. To achieve full functionality of an electronic device or component, the design process must first involve visualizing physical properties, designing materials at the atomic level, and ensuring that all materials' physical properties will be retained in the final product.

Kobe Steel began developing electronic materials in the 1980s, starting with magnetic sputtering target materials for magneto-optical recording media.[1] Subsequent expansion incorporated diamond thin films and devices[2] as well as aluminum electrodes used in semiconductor manufacturing equipment.[3] Our sputtering target materials used for thin-film formation have expanded into reflective materials for optical recording media, aluminum alloy wiring materials for flat panel displays (FPDs), and oxide semiconductor materials. Design factors must support both the properties of electronic materials at the atomic level and the properties of electronic devices and components provided to the end user.

Fig. 1 shows Kobe Steel's electronic materials development methodology and related fundamental technologies. Material manufacturers have typically supplied electronic materials directly

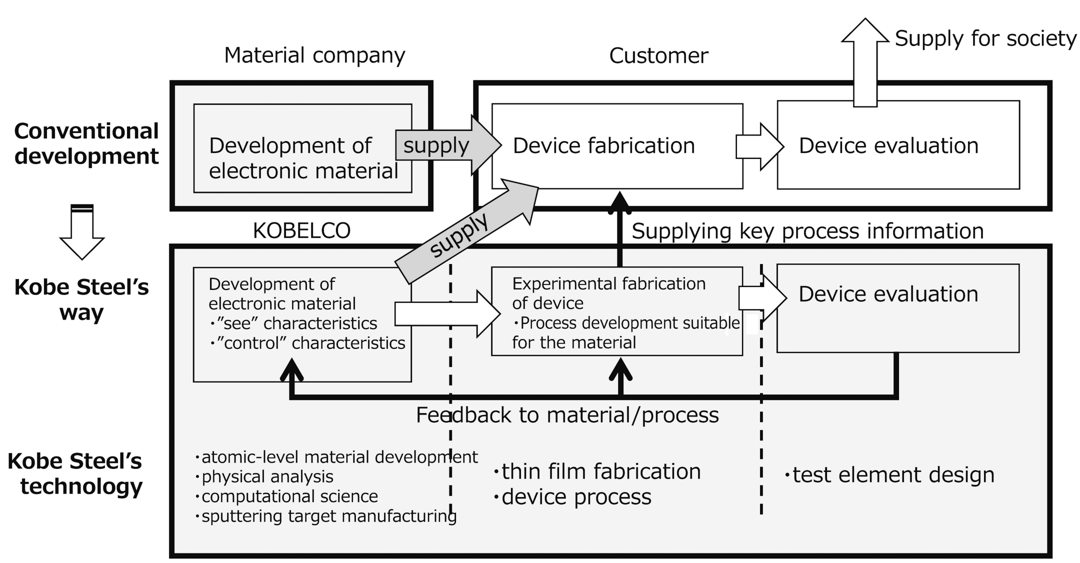

Fig. 1 Kobe Steel's R&D process for electronic materials and technologies

to manufacturers of devices and components, who in turn use these materials to produce and evaluate electronic devices. The electronic device manufacturing process must not degrade materials' physical properties. When a customer's product does not achieve the desired characteristics, it can be challenging for the material manufacturer to determine whether the problem lies in the manufacturing process or in the material itself. In such cases, material manufacturers must have highly effective evaluation capabilities and the ability to evaluate products from the user's perspective.[4] Therefore, as depicted in Fig. 1, Kobe Steel developed an in-house environment for prototyping and evaluating electronic devices at the customer's site, enabling us to evaluate whether the characteristics of an electronic device are satisfactory. Our method distinguishes whether the root cause of a given defect lies in the material or the manufacturing process. Our method also involves determining and communicating the manufacturing processes and conditions that are critical to the functionality of the customer's electronic materials. These practices can greatly condense the time needed to optimize the manufacturing conditions for an electronic device.

This paper outlines Kobe Steel's fundamental technologies and method logies supporting the development of electronic materials. Outlined as well are examples of applications that have entered mass production, including oxide semiconductor materials for FPDs as well as recording film materials for optical disks.

1. Fundamental technologies supporting electronic material functions

This section introduces the fundamental technologies supporting electronic material functions, followed by various application examples. The bottom portion of Fig. 1 depicts Kobe Steel's R&D process for electronic materials, which leans on certain fundamental technologies to develop electronic materials and to prototype and evaluate electronic devices.

1.1 Electronic materials development

As shown on the left side of Fig. 1, the fundamental technologies required for the development of electronic materials involve atomic-level material design, physical analysis, computational science, and sputtering target manufacturing. Critical here is the visualization of physical properties, which can be achieved through physical analysis and computational science. Some physical analysis techniques center around defects that can be observed directly, such as in atomic arrangements; others analyze electrically active defects, such as those in defect levels. Computational science, based in particular on first-principles calculations, is also becoming increasingly important for analyzing physical properties that are difficult to measure or observe directly.

Fig. 2 depicts the defect analysis of an oxide semiconductor material via PITS (photoinduced current transient spectroscopy) as an example of the visualization of physical properties. Although the PITS analysis method[6), 7)] is omitted, Fig. 2(b) shows the results of the PITS analysis performed on a test element as shown in Fig. 2(a). The vertical axis of Fig. 2(b) correlates to the defect density; the horizontal axis indicates the temperature, which corresponds to the activation energy. This analysis was the first in the world to investigate the band structure of an oxide semiconductor material as shown in Fig. 2(c), including an analysis of which defects were caused by constituents such as Zn versus which were caused by the manufacturing process involving constituents such as hydrogen surrounding the oxide semiconductor material.

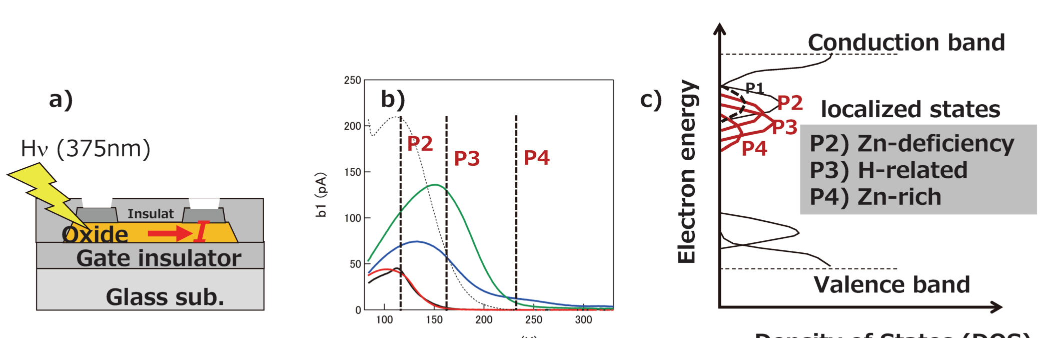

Fig. 2 Example of PITS analysis[5), 6)] – a) Test element for PITS, b) Comparison of PITS results with different test element fabrication processes, c) Band structure diagram deduced from PITS analysis

1.2 Prototyping and evaluation of electronic devices

Kobe Steel is a material manufacturer with the unique device prototyping and evaluation technologies necessary to determine whether an electronic device is acceptable. Electronic devices often comprise several layers of thin films, with prototypes being fabricated via thin-film formation technology and photolithography (a process that establishes alternating layers of photoresists and etched patterns). Kobe Steel has the equipment and clean rooms necessary to produce layers of thin films, accomplished by repeating the photolithography process. The broad spectrum of electronic devices manufactured at customers' sites includes transistors, sensors, organic EL devices, and optical storage media. Kobe Steel can create custom prototypes, which differ in terms of the type and structure of the device and the composition and pattern of the device's thin films.

Fig. 3 shows an example test element for TFT (thin-film transistor) evaluation. Fig. 3(a) shows the cross-section of a TFT; Fig. 3(b) shows the TEG (test element group) of a prototype TFT on a glass wafer. The TEG demarcates various characteristics, which is necessary for effective electronic device evaluation.

Properties involved in the evaluation include the dependence of electrical resistivity on linewidth, the dependence of contact resistivity on contact area, and the dependence of transistor current-voltage characteristics on gate length. The shape and structure of the elements are custom-designed according to what is being evaluated. A single wafer contains elements with different structures. Thus, as with device prototyping, TEGs are designed according to what is to be evaluated.

2. Example applications of functional electronic materials technology

This section covers oxide semiconductor materials for FPDs and recording film materials for optical disks as prime examples of functional electronic materials technology.

2.1 Development of oxide semiconductor materials for FPDs

FPDs are an essential element of electronic devices such as smartphones and tablets. Recent years have seen a demand for higher image resolution, reduced power consumption, and support of foldable and wearable devices. To support such needs, the KOBELCO Group has developed an oxide semiconductor material (In-Ga-Zn-Sn-O: IGZTO) that FPD manufacturers are already using in mass production.

Professor emeritus Hideo Hosono of the Tokyo Institute of Technology developed an amorphous oxide semiconductor material (In-Ga-Zn-O:IGZO)[8] featuring a high electron mobility of 8 cm^2/Vs and an extremely low leakage current owing to its wide band gap. It is now widely used in the transistors used as switches for FPD pixels. The miniaturization of transistors enabled by increased electron mobility brings great advantages, such as higher resolution and narrower bezels. Such capabilities have led FPD manufacturers to demand our materials with increasing frequency. However, a technological breakthrough is needed to overcome the trade-off between greater mobility and reduced reliability.[9]

Fig. 4 compares Sn-free IGZTO with Kobe Steel's Sn-doped IGZTO. Fig. 4(a) shows the relationship between drain current and gate voltage. Good switching characteristics, in which the drain current flows above a certain gate voltage, were observed. However, long-term excitation of the device with light at a wavelength of 375 nm caused a negative threshold voltage shift (see the results of the NBTIS reliability test for details).[10] Adding Sn clearly suppresses the threshold shift. The large number of P2 and P3 defects, depicted in Fig. 2(c), caused this threshold shift, meaning that suppressing these defects is key. In the process of researching materials, PITS analysis revealed that Sn doping suppresses Zn-related defects (P2) and

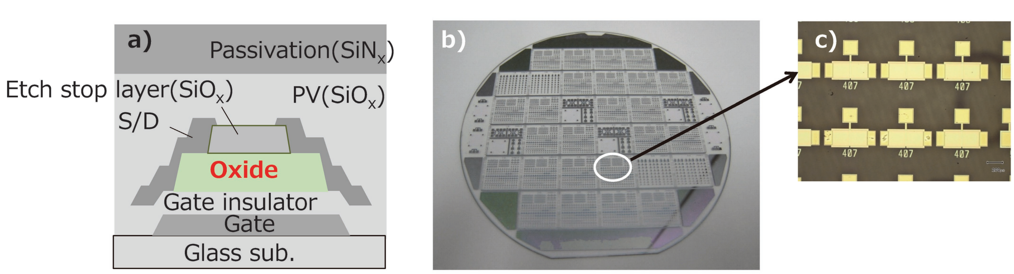

Fig. 3 Example of test element design for thin-film transistor (TFT) evaluation – a) Cross-section of TFT, b) Test element for TFT evaluation on 6-inch glass, c) Optical microscope image of TFT

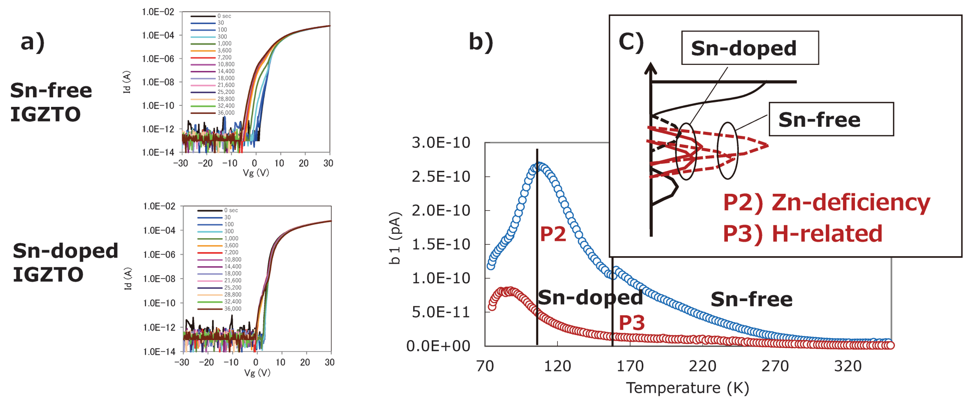

Fig. 4 Transfer characteristics of Kobe Steel's Sn-doped IGZTO TFTs - a) NBITS test (upper: Sn-free, lower: Sn-doped IGZTO), b) PITS analysis (blue: Sn-free, red: Sn-doped IGZTO), c) Band structure diagram of IGZTO deduced from PITS

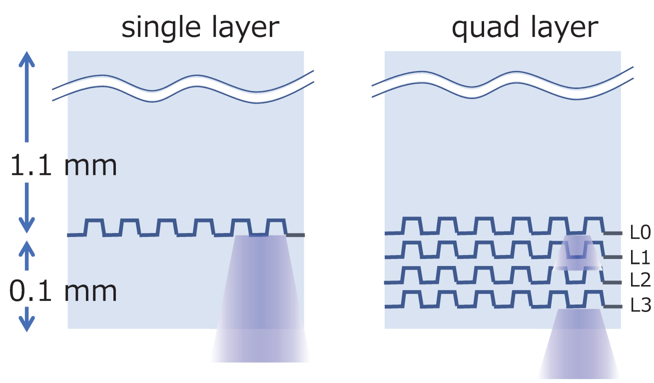

Fig. 5 Structure of single-layer disk and quad-layer disk

that Sn doping alongside optimization of production processes with hydrogen suppresses H-related defects (P3). As shown in the analysis depicted in Fig. 4(b), adding Sn reduces the defect density (vertical axis), enabling defect control as shown in the band structure diagram (Fig. 4(c)) deduced from PITS. The threshold shift of Sn-doped IGZTO is suppressed to an amount unproblematic even in mass production, and an electron mobility of 29 cm^2/Vs-more than three times that of conventional IGZO-is achieved.[11] Critical as well is the optimization of manufacturing processes involving hydrogen. As such, we shared this information with FPD manufacturers (the direct consumers), which led to the expeditious adoption of the technique.

2.2 Development of recording film materials for optical disks

The trend toward digitization has led to a massive leap in the amount of data requiring long-term storage. Optical disks and conventional magnetic tape present options for such storage, but increased disk capacity is needed. The recording capabilities of optical disks have expanded to include CDs, DVDs, and Blu-ray discs. Recordable disks such as CD-R, DVD-R, and BD-R have a recording film whose optical properties change when heated by a laser. Although the recording film can be made of various organic dyes and phase-change materials, either option requires a reflective layer of aluminum alloy or silver alloy to collect the incident laser beam as a signal. **Fig. 5** shows the structure of a single-layer disk and a multilayer (quad-layer) disk. One way to increase recording capacity is to establish multiple recording film layers. However, the reflective layer prevents light from reaching deeper layers, making it difficult to record to these deeper layers. As such, new structures and materials must be innovated.

To meet this need, Kobe Steel researched oxide materials as inorganic materials that allow for reading and writing, decompose when heated, and have a high refractive index and low extinction coefficient. Our research culminated in the development of a new palladium oxide material.[12] **Fig. 6**(a) shows the XPS analysis of unrecorded and recorded areas to visualize the oxidation

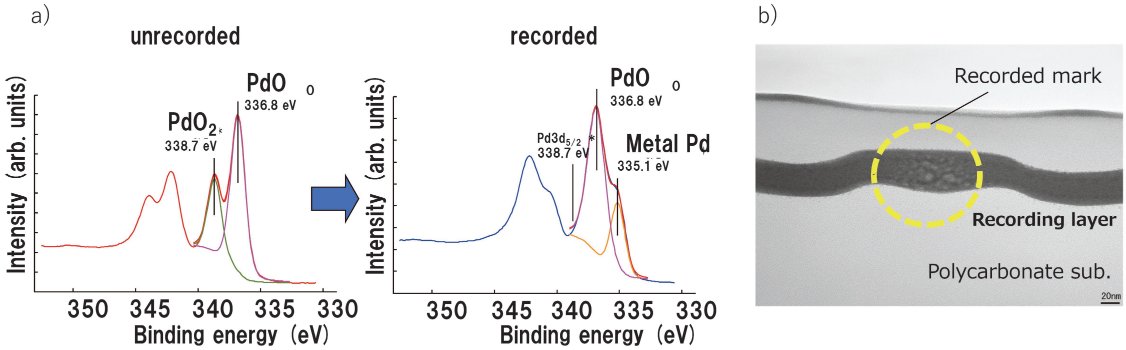

Fig. 6 XPS analysis of unrecorded and recorded areas and TEM cross-section of recorded disk – a) XPS analysis, b) TEM cross-section

state of PdO_2. The unrecorded area contains PdO_2, a peroxide formed by reactive sputtering. After recording, PdO_2 is absent and metallic Pd is present. This indicates that the laser's heat decomposes the PdO_2, reducing it to metallic Pd. This transformation alters the optical properties. Furthermore, direct observation via cross-sectional TEM (Fig. 6(b)) confirmed that the recorded area has a porous structure and has undergone volume expansion because of the release of oxygen from the decomposition of PdO_2. The transformation from oxide to metal changes the optical properties, which constitutes the mechanism behind recording. Another aspect of the mechanism is the change in reflectance after recording, which occurs because of the optical interference caused by expansion and morphological change within the layer.

Recording film materials must meet certain optical and chemical parameters, ensure good signal characteristics, and exhibit resistance to environmental influence. This is what drove us to introduce media manufacturing techniques and signal characteristic evaluation technology in support of materials development. **Fig. 7** graphically depicts the relationships between writing power and jitter[13] in the various materials studied. Jitter is the standard deviation of the recorded signal's rise and fall time from a reference frequency; the lower the jitter, the better the signal. We created a single-layer disk as a test element in house (Fig. 5, left), evaluated the jitter, and developed a recording film material with a favorable composition. The customer subsequently conducted film formation, disk production, and signal characteristic evaluations and successfully reproduced favorable characteristics. The material developed then saw practical application as a recording film material in multilayer Blu-ray discs.

This is a prime example of how we provide easy-to-use materials through comprehensive materials research, visualization of physical properties through atomic-level analysis, and verification of device characteristics using in-house test elements for evaluation.

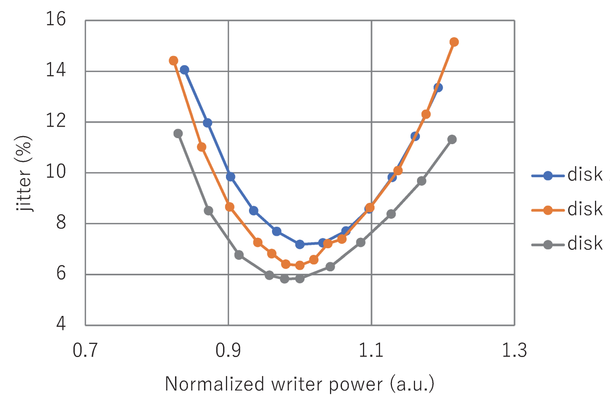

Fig. 7 Various materials' relationships between signal quality and writing power

Conclusions

IoT expansion is dramatically increasing the number of electronic devices in use. As such, materials that improve device performance are increasingly critical. Materials provided must not simply maintain device- and component-level properties, but rather must maximize their expression in support of device functionality.

Kobe Steel's functional electronic materials technology will continue to ensure the comprehensive development of electronic materials and devices, including design, manufacture, prototyping, and functional property evaluation. We will furthermore continue providing materials that electronic device manufacturers and end users alike can use safely and confidently.

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