Analysis of thin films and interfaces

Recent advances in analytical techniques let us measure the properties and control the quality of microstructures and let us use them to study novel physical phenomena.

John M. Poate and King-Ning Tu

The preceding articles in this special issue amply demonstrate the crucial role that thin films play in present-day science and technology. These films can now be fabricated routinely and their application in advanced technologies is assured. To control the quality of the films and to measure their behavior we must develop techniques that can make measurements on minute quantities of material with dimensions of fractions of a micron. We need to determine the crystal structure, the chemical composition and the microstructure of the films. In the past five years or so, we have seen the realization of analytical techniques that give detailed information on thin-film structures, information that was not accessible with earlier analytic techniques.[1]

Some of the most important applications of thin films occur in microelectronics, and we will illustrate the development of the subject from this field. The films are typically in multilayered structures, whose dimensions are clearly shown in figure 1: a transmission electron micrograph of a (transverse) section of a polycrystalline-silicon gate field-effect transistor.[2] In general, we are concerned with films ranging in thickness from a few hundred angstroms to several microns with lateral dimensions that are now less than 1 micron. No single technique is capable of supplying all the requisite information on film composition and structure. Some techniques probe composition and structure deep within the layers of material, others probe only the outermost surface. A clear picture of a microstructure composed of thin films can only emerge from a combination of analytic techniques.

Analytic techniques

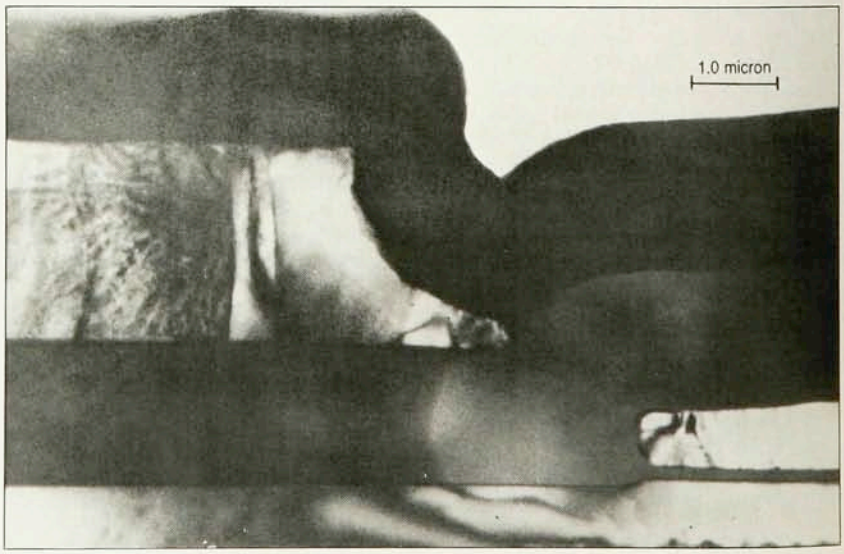
We can classify analytic techniques according to the properties to which the probes are most sensitive:

- the composition of the films
- their crystalline structure
- the surface morphology of the microstructure
- composition and chemical structure at the submicron level
- interface structure and composition

In some cases, such as transmission electron microscopy, the techniques can be adapted to different uses, but the analysis of each type of property has its own problems and its own solutions.

One can determine the composition of layers of thin films with Rutherford backscattering, with sputter erosion combined with Auger-electron spectroscopy or secondary-ion mass spectroscopy or with electron microprobes. Because nuclear elastic-scattering cross sections are well understood, Rutherford backscattering of energetic ions—energies in the MeV range—is an extremely accurate probe for determining composition as a function of depth. This technique has made possible analyses of films up to several microns thick with a depth resolution of several hundred angstroms. Auger electrons and secondary ions arise only from the surface, but their energies depend on the chemical composition of the surface. By using low-energy ion beams to erode the surface layers in sequence, one can use these surface-analytic techniques to determine composition as a function of depth. The equipment for these surface techniques is widely available, so they are popular for depth-dependent analyses as well. Their fine lateral resolution is an additional advantage.

The traditional tool for determining crystalline structure is x-ray diffraction. Transmission electron microscopy can also provide information about crystal structure; because electrons can be focussed, they can provide information about very small structures. Ion-channeling measurements, in which one



Field-effect transistor: a transmission electron micrograph of a cross section through an insulated-gate field-effect transistor. (Courtesy of T. T. Sheng, Bell Laboratories.) Figure 1

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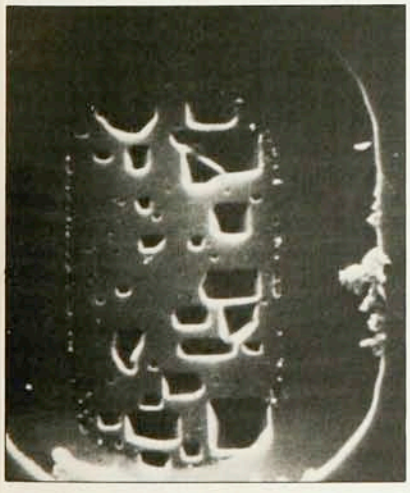
determines the enhancement of transmission of ions in preferred directions through a crystal lattice, also provide a probe of crystal structure.

To determine surface morphology one generally uses scanning electron microscopy. By making a replica of the surface and shadowing it with heavy metals one can also use transmission electron microscopy to examine the shape of the surface. To examine the samples with visible light, one uses Nomarsky microscopy, which is a form of reflection interference microscopy.

Scanning Auger-electron spectra and scanning transmission electron microscope data are both sensitive to chemical composition and structure, and both have submicron lateral resolution. One can, in fact, make detailed maps of surface composition using scanning Auger-electron spectroscopy.

Information about the structure and composition of the interfaces between films can be obtained in several different ways. Transmission electron microscopy of cross sections of devices (as, for example, shown in figure 1) gives information about interfaces as well as the layers themselves. Rutherford backscattering and ion channeling, similarly, provide information about the composition and structure, respectively, of interfaces as well as films. In situations in which the interfaces can be examined layer by layer—either by sputter erosion or by monolayer deposition—surface techniques, particularly Auger-electron and photoelectron spectroscopy, are useful.

Rather than consider in detail the capabilities of these techniques, we will instead discuss several current areas of thin-film research that illustrate the usefulness of several techniques. We are here dealing with unique structures whose behavior in terms of thermal stability and reactivity are very different from bulk structures. Moreover, many of the properties of interest are not associated with the film, *per se*, but with its interface with the substrate or underlying film. It is only recently that one has been able to observe directly the structure or composition of interfaces. We will give specific examples of particular techniques; however, we should emphasize that a useful analysis of thin films and interfaces requires a combination of techniques.



Scanning electron micrographs of aluminum-silicon contacts after alloying at 400 °C. The aluminum has been etched away, but the SiO_2 that covers most of the silicon (except for the contact) remains. The width of the contacts is 10 microns. (Courtesy of T. M. Reith, IBM Data Systems Division.) Figure 2

Contacts to silicon

Transistors cannot function without electrical connections to the outside world. Such a connection in its simplest, conducting form is referred to as an ohmic contact; if the connection acts as rectifier it is called a Schottky barrier. In microelectronic devices, these two kinds of contacts are made by depositing and reacting a thin metallic film on semiconductors; a typical example is an aluminum contact on a silicon wafer. Any good metal-to-semiconductor contact requires a limited and uniform reaction at the contact interface. A reaction that is too strong or nonuniform may produce a deep contact that—in the case of a transistor or diode, for example—penetrates the underlying p–n junction. On the other hand, the reaction must be strong enough to produce a good contact in spite of the native oxides and chemical contaminants (from cleaning and etching) that cover the surface before the reaction; such impurities tend to cause undesirable effects at the interface.

In the case of aluminum on silicon, the reaction is strong and not uniform, producing deep pits where aluminum penetrates into silicon. Figure 2 shows an example of these pits; the larger pits are somewhat more than a micron across. Such pits were tolerated in the early integrated circuits, because the circuit elements were larger than ten microns, but the pits became intolerable as the devices became smaller. Clearly, in a circuit with critical dimensions around one micron, the larger pits shown in figure 2 can cover an entire contact.

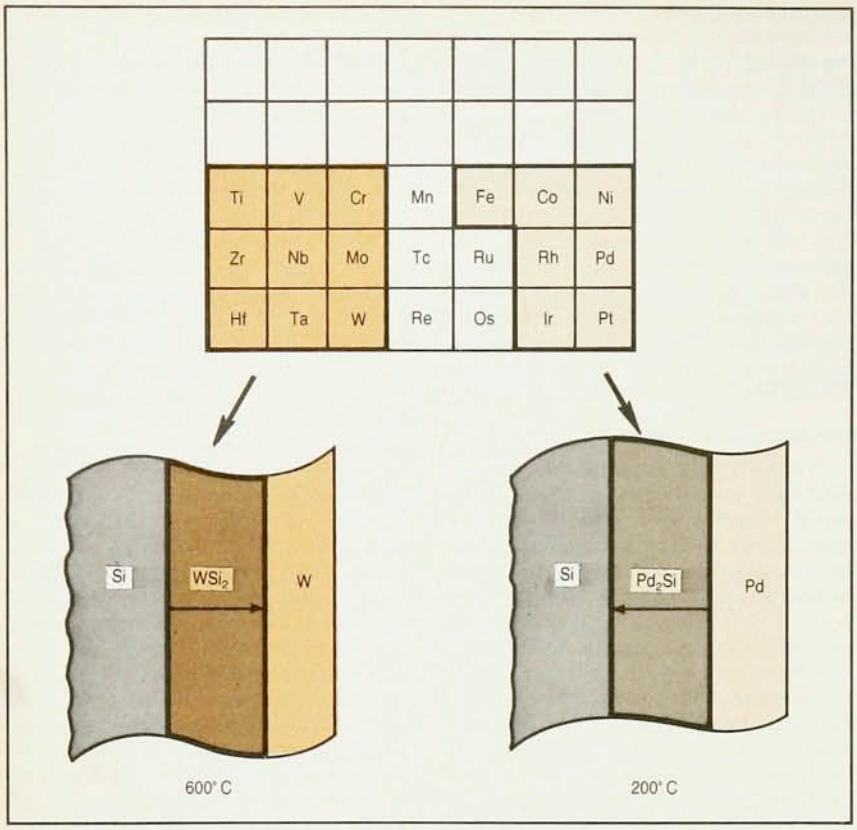
To avoid this contact problem, some laboratories introduced silicide films of PtSi or Pd_2Si between the aluminum and silicon to serve both as an atomic diffusion barrier and as a contact layer.[3] This technique has provided an impetus to study silicide formation and physical properties of silicide–silicon interfaces. These studies have benefited from a combination of analytical techniques, such as Rutherford backscattering, glancing-incidence x-ray diffraction, transmission electron microscopy and Auger-electron spectroscopy.

Silicide contacts are formed by reacting thin metal films with silicon. During the reaction the metal or the silicon diffuses into the other material, forming the silicide compound. Which species—silicon or metal—is the dominant diffusing species affects important technical considerations; in general it is preferable that the metal atoms dominate. When the metal atoms diffuse into the silicon, the silicide–silicon interface is clean and free from the native-oxide contaminants of the silicon surface. If silicon diffusion predominates, vacancies flow towards the interface, forming voids and thus reducing the contact area and producing poor mechanical properties. It has also been observed that the reaction temperature depends on the diffusing species: Metal-atom diffusion leads to silicide formation at low temperatures while silicon-atom diffusion leads to a high temperature of formation.

To determine which is the diffusing species, we have used[4–6] tiny bubbles of xenon (formed by ion implantation at the silicon–metal interface) as immobile, non-diffusing, markers. The energy of ions (2-MeV helium ions, for example[4]) backscattered from the xenon atoms depends on how much energy the ions lose in the overlying material, so that the position of the peak due to xenon in the spectrum of backscattered ions is a measure of the depth of material above the xenon. Before diffusion and silicide formation, the xenon peak is at an energy determined by the helium ions' energy loss in the metal film. After the reaction, the energy of the peak shifts, even though the xenon atoms do not move: If the metal has diffused into the silicon the xenon layer is exposed at the surface, so that the energy of the backscattered ions is higher than before. On the other hand, if the silicon diffuses into the metal film, the xenon layer is embedded even deeper in the device, and the ions' energy loss is greater than before diffusion and silicide formation.

The transition-metal silicides we have studied show a surprisingly systematic behavior. As figure 3 indicates, the near-noble metal silicides form at a relatively low temperature, around 200 °C; they are metal rich; and their formation is dominated by metal-atom diffusion. The refractory metal silicides form only at high temperature, near 600 °C; they are silicon rich, and their formation is dominated by silicon-atom diffusion. The correlation between formation temperature and

John Poate is at Bell Laboratories in Murray Hill, New Jersey; King-Ning Tu is with the IBM Thomas J. Watson Research Center in Yorktown Heights, New York.



Silicide formation. This segment of the periodic table shows (light color) those elements that form silicides by silicon diffusion and at high temperatures and (dark color) those elements that form silicides by metal diffusion and at low temperatures. Figure 3

the diffusing species is intriguing. The reason for the correlation may lie in the solid-state processes necessary to break atoms of silicon loose from the substrate to feed these reactions.[7]

Silicide structure

Some of the silicides can be made to grow as epitaxial films, that is, as films whose crystal structure is governed by the underlying silicon structure. But whereas most epitaxial films are produced by simple deposition on a compatible host substrate, silicide epitaxy is, as we have discussed, the result of mass transport and chemical reaction. It is perhaps surprising that these circumstances lead to good epitaxy.

Recent experiments have permitted direct observation of the silicon–silicide interface. Nickel di-silicide, with the cubic CaF_2 structure, has almost exactly the same lattice parameter as silicon. Figure 4 shows a high resolution lattice-imaging transmission electron micrograph of a $NiSi_2$–Si interface. Each lattice fringe spacing corresponds to a lateral resolution of 3.1 Å. The interface is marvelously uniform. In fact, the $NiSi_2$ epitaxy is so good that we have used helium-ion channeling to examine the continuity of the crystal structure across the interface.[8] (In channeling experiments one measures the energy and intensity of backscattered helium ions.) With the crystal in a random orientation the resulting spectrum gives the composition of the film as a function of depth, as we mentioned earlier. With the crystal aligned in the ⟨111⟩ direction, the backscattering is greatly reduced, because the helium atoms can penetrate deeply into the crystal without encountering scattering atoms. In the case of the $NiSi_2$–Si epitaxial crystal, the backscattering spectrum shows only narrow peaks arising from surface atoms of nickel and silicon; there are almost no helium atoms scattered from within the crystal, not even from nickel atoms misaligned at the interface between the two crystals. The absence of such a peak indicates that any disorder due to the interface must extend over less than a few atomic monolayers.

The properties of the interface are strongly affected by the technique used to deposit the thin films. Low-energy-ion bombardment of the substrate is one of the techniques being explored; it has already been used to produce interesting silicide layers. Our cover shows a dual-ion-beam system that provides a great variety of interface conditions and growth environments. One of the two ion beams is focussed onto a target (made from material to be formed into a film) and removes atoms from it by sputtering. Some of these target atoms condense onto the substrate for the film, thus forming the film. The second ion beam can be used to bombard the substrate to clean its surface, to produce local atomic mixing at the interface or to modify the growth conditions for the film. By using reactive gas ions in the second beam one can deposit films of compounds such as oxides or nitrides. The dual-ion-beam system is also useful for studying the process of sputtering in alloys,[9] particularly for studying the changes in surface composition during sputtering, an important process both in preparing contact surfaces and in controlling the composition of deposited films.

It will be interesting to see how the structure and composition of the interface correlate with an electronic property, such as the Schottky barrier height (the potential barrier for injecting electrons from the metal into the semiconductor). One useful approach[10] is to combine photoelectron spectroscopy (uv and x ray), Auger-electron spectroscopy and high-resolution transmission electron microscopy to study band structure and electronic interaction at the very early stages of silicide formation.

Another important area of research involves fabrication of shallow metal–semiconductor contacts for application in very-large-scale integrated devices. The advances in device miniaturization demand a scaling down of vertical dimensions, to the point where contacts about 100 Å deep are required. As we mentioned, direct metal–silicon contacts give rise to problems, some of which can be reduced by an interposed silicide layer. The metal-silicide interface may require still further protection, however. One recent, successful approach to manufacturing such shallow contacts makes use of a second protective layer, as shown in the figure on page 47. By depositing[11] an alloy film such as Pd–W and raising the temperature to 400 °C one forms Pd_2Si with palladium that has migrated from the alloy; the remaining, unreacted tungsten provides a protective layer between the thin layer of silicide and the aluminum contact line.

Amorphous silicon films

Because of their possible uses—for example in photovoltaic cells or for the growth of epitaxial silicon—amorphous-silicon films produced by vacuum deposition are attracting considerable attention. Another kind of amorphous-silicon film is produced on the surface of crystalline silicon when one uses ion implantation to introduce dopants, such as boron, phosphorus or arsenic into the crystal. Ion implantation frequently makes the outermost

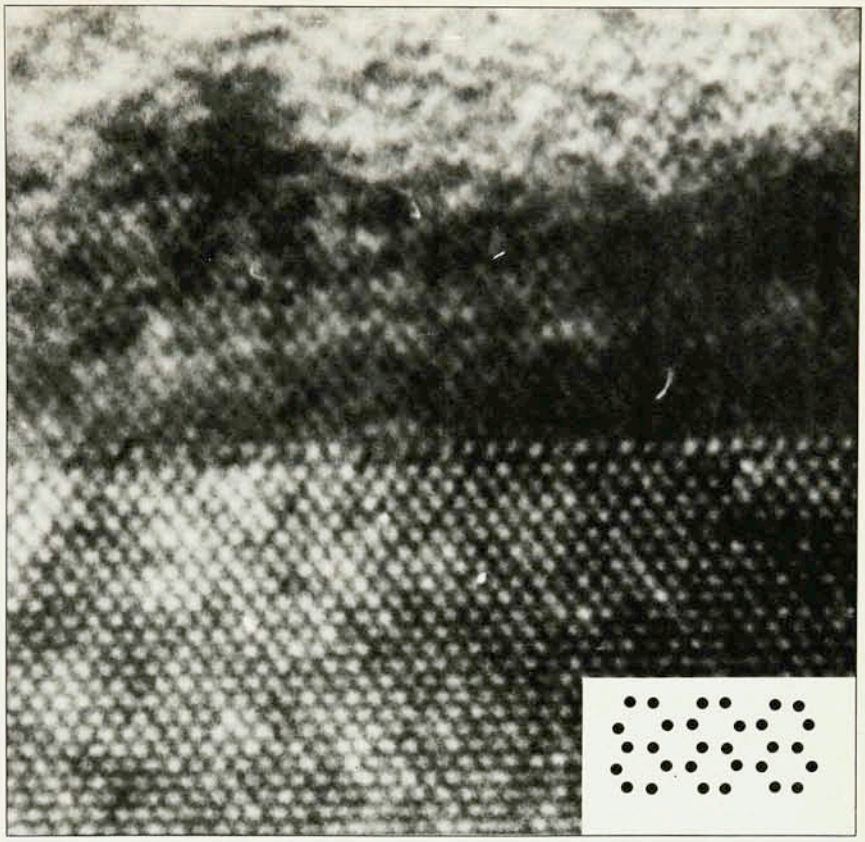
silicon layers amorphous; the crystal structure is restored by heating the material in a furnace. A group at the California Institute of Technology has studied[12] the epitaxial regrowth of these amorphous layers using Rutherford backscattering and ion channeling. Figure 5 shows a series of channeling spectra of an amorphous silicon layer on a single crystal of silicon, taken at various times as the sample was held at 550 °C. The spectra show clearly the effects of the epitaxial regrowth of the crystal: As the crystal grows, the amorphous layer becomes thinner and fewer ions are scattered from any but the outermost atoms.

Studies such as these have led to a better understanding of the epitaxial regrowth phenomenon. The epitaxial regrowth of deposited silicon films is quite different from that of implanted amorphous films;[13] it is, for example slower and not linear with time. The difference has been attributed to structural differences between implanted and deposited amorphous films and to the higher levels of impurities in the deposited films.

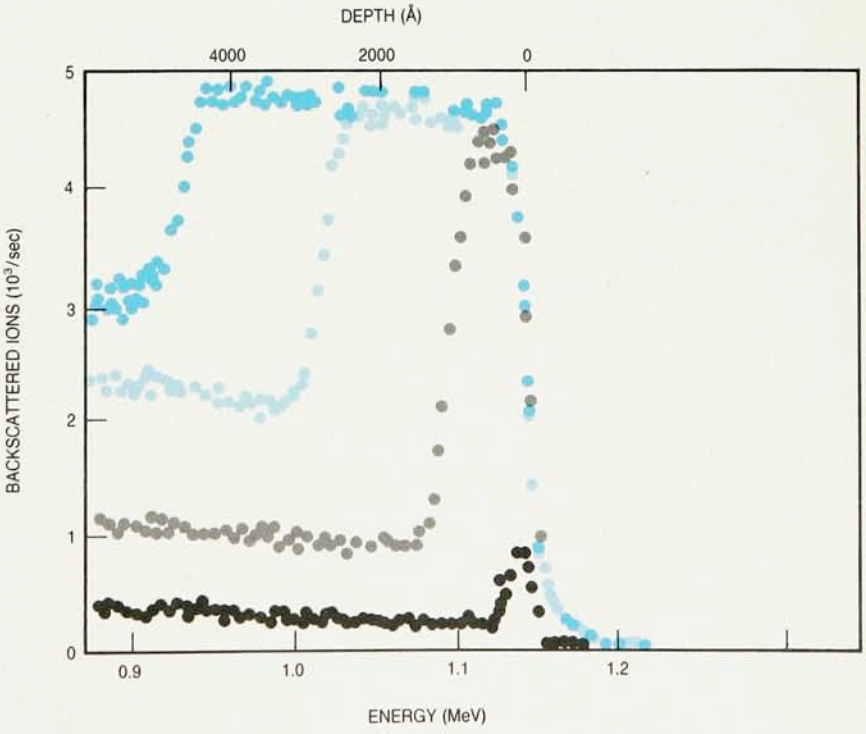
Instead of heating the entire crystal in an oven for relatively long times, some groups have recently used laser-heating to induce recrystallization of amorphous silicon layers.[14] (See PHYSICS TODAY, July 1978, page 17.) The amorphous layer crystallizes in times on the order of 0.1 to 1000 *microseconds*. The new thin-film analytic techniques have made it possible to study this novel regime of crystal growth in some detail.

Microanalysis

In parallel with the trend towards microfabrication, there is a current trend of analytical research towards microanalysis, that is, the ability to determine the composition and structure of tiny material aggregates, 10 Å to 100 Å in scale. Within the past few years, there have been substantial developments in this area, such as field-ion microscopy and scanning transmission electron microscopy. One basic requirement of microanalysis is to have a lateral resolution of the order of atomic dimensions. Such high resolution is not achievable with most available techniques. In fact, such techniques as glancing-incidence x-ray diffraction and ion backscattering often sacrifice lateral resolution to gain depth resolution. Other requirements for microanalysis are high intensity and an ultra-high vacuum environment. The new scanning techniques that make use of finely focussed incident beams, however, can achieve the required resolution. Scanning transmission electron *microscopy* can produce analyses for extremely small samples. A commercially available system



Silicon–silicide interface. This high-resolution transmission electron micrograph shows the interface between silicon and nickel di-silicide. The inset shows a schematic view of this plane of the crystal lattice; the white dots in the micrograph correspond to open channels in the lattice. (Courtesy of H. Foell, IBM Research.) Figure 4



Epitaxial regrowth of silicon. The graphs show backscattering spectra of 2-MeV helium ions from the ⟨100⟩ surface of a silicon crystal implanted, at liquid nitrogen temperatures, with silicon ions. The sample was pre-annealed at 400 °C for an hour and then annealed at 550 °C for the times indicated. (From reference *12*.) Figure 5

for scanning transmission electron micrography that contains a field-emission electron gun can deliver a beam 5 Å in diameter and sufficiently bright to analyze an aggregate of 1000 atoms in a vacuum of 10^{-9} torr.

The developments we have discussed make it possible to monitor the quality of microstructures containing thin films. These films can now be fabricated routinely and their application in advanced technologies can be assured. Quality control is probably the most important contribution of thin-film analysis. Many of the unique properties of thin-film microstructures can also now be used for the study of specific or novel physical phenomena. For example, one can now study the possibility of attaining high superconducting transition temperatures in thin films of materials that cannot be fabricated in bulk form; one can observe quantum states in thin-film superlattices, and new types of conduction phenomena in fine metallic lines. We believe that the field of thin-film analysis and research is still in its infancy and that the future will bring many exciting developments in this submicron world.

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