Radioactive silicon as a marker in thin-film silicide formation*

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(Received 17 January 1977; accepted for publication 4 March 1977)

A new technique using radioactive ^{31}Si (half-life = 2.62 h), formed in a nuclear reactor, as a marker for studying silicide formation is described. A few hundred angstroms of radioactive silicon is first deposited onto the silicon substrate, followed immediately by the deposition of a few thousand angstroms of the metal. When the sample is heated, a silicide is first formed with the radioactive silicon. Upon further silicide formation, this band of radioactive silicide can move to the surface of the sample if silicide formation takes place by diffusion of the metal or by silicon substitutional and/or vacancy diffusion. However, if the band of radioactive silicide stays at the silicon substrate interface it can be concluded that silicon diffuses by interstitial and/or grain-boundary diffusion. This technique was tested by studying the formation of Ni_2Si on ⟨100⟩ silicon at 330°C. From a combination of ion-beam sputtering, radioactivity measurement, and Rutherford backscattering it is found that the band of radioactive silicide moves to the surface of the sample during silicide formation. From these results, implanted noble-gas marker studies and the rate dependence of Ni_2Si growth on grain size, it is concluded that nickel is the dominant diffusing species during Ni_2Si formation, and that it moves by grain-boundary diffusion.

PACS numbers: 68.55.+b, 66.30.Fq, 82.55.Kq

There is much interest in the formation of thin-film metal silicides, because of their importance as contact layers in silicon devices. Identification of the dominant diffusing species and its diffusion mechanism is crucial to a fuller understanding of silicide growth.

Implanted rare gases such as Xe and Ar have been successfully used as diffusion markers in thin-film studies and the diffusing species determined during Ni_2Si,[1,2] Mg_2Si,[3] FeSi,[3,4] $TiSi_2$,[2,3] and VSi_2[2,3] formation. Such markers should ideally be inert and should remain immobile as the diffusing species streams by. The marker is usually implanted into the Si before deposition of the thin metal layer. The position of the marker after silicide formation is then determined by Rutherford backscattering of ^4He particles having an energy of a few MeV. If the metal is the dominant diffusing species, the marker will shift towards the surface of the sample, while a displacement deeper into the sample indicates silicon diffusion during silicide growth. The use of implanted noble atoms as diffusion markers does however have some inherent disadvantages.

(1) The introduction of foreign atoms into the system could affect the mechanism of silicide formation and the kinetics.

(2) Radiation damage introduced during marker implantation may also influence silicide formation and should first be removed by appropriate annealing.

(3) Solubility effects could cause dragging of the marker at the interface, thereby giving erroneous results.

(4) The choice of marker elements and of silicides which can be studied is restricted because backscattered particles from the marker must be distinguishable from those particles scattered from silicon and metal atoms.

(5) The technique only gives information about mass movement past the marker. No information is obtained about the mechanism of the diffusion process.

In this work a new technique using radioactive Si atoms as a marker is described and its merits and disadvantages compared with implanted markers are discussed.

Radioactive silicon can be formed by thermal neutron irradiation of silicon in a nuclear reactor. The only relatively long-lived radioisotope formed from silicon during neutron activation is ^{31}Si by the reaction $^{30}Si(n,\gamma)^{31}Si$. This radioisotope is a β emitter which decays with a half-life of 2.62 h and can readily be measured with a β-counter. Because of the high degree of purity of semiconductor-grade silicon, no interfering activities are formed. Activities from surface contamination must however first be removed by etching the silicon in a $HF:HNO_3$ solution after neutron activation.

For a marker experiment, a few hundred angstroms of radioactive silicon are deposited onto a silicon substrate by electron-gun evaporation in vacuum, followed immediately by deposition of a few thousand angstroms of the appropriate metal. From Fig. 1 it can be seen that when the sample is heated, a silicide is first formed with the radioactive silicon. When all the radioactive silicon has reacted with the metal we have a band of radioactive silicide between the silicon substrate and unreacted metal. Upon further silicide formation this band of radioactive silicide can for example move towards the surface of the sample or it can remain at the single-crystal interface depending on the diffusing species and its mechanism of diffusion during silicide formation. In Fig. 1 the position of the radioactive marker is shown for different modes of diffusion of the metal or silicon atoms. Apart from these two limiting cases the marker could be located somewhere in the middle of the silicide layer if silicide formation takes place by interstitial or grain-boundary diffusion of both

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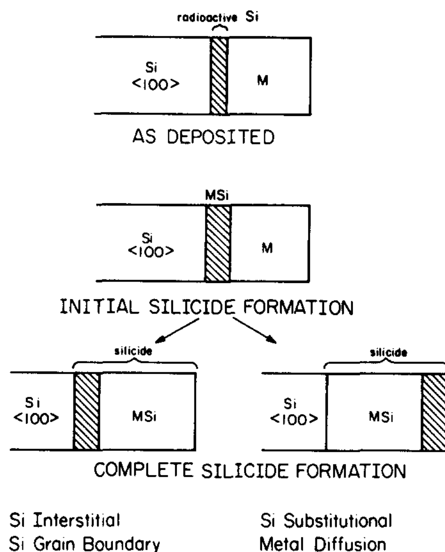

FIG. 1. Schematic diagram showing how radioactive silicon can be used to determine the diffusing species and its mechanism of diffusion during silicide formation. (M = metal). If the metal is the diffusing species its mechanism of diffusion can only be determined if a radioactive metal tracer is used. If the activity is observed somewhere in between the two limiting cases shown here, then interstitial and/or grain-boundary diffusion of both the metal and silicon probably occurs simultaneously.

the metal and silicon atoms, the exact position depending on the relative diffusion rates of both species.

We have used this new radioactive marker technique for studying Ni_2Si formation. About 200 Å of radioactive silicon was deposited on single-crystal silicon wafers (about 1 cm^2 in size), with polished surfaces and ⟨100⟩ orientation, by electron-gun evaporation in vacuum, followed immediately thereafter by the deposition of a few thousand angstroms of Ni. Samples were then annealed in vacuum at 330 °C for 20 min. Rutherford backscattering showed that only the first phase, Ni_2Si, had formed under these conditions. Profiling of the radioactive marker was then carried out by a combination of ion-beam sputtering, radioactivity measurement, and Rutherford backscattering. For an Ar ion-beam energy of 2 keV and a beam current of 10 mA, approximately 110 Å of Ni_2Si was removed per minute. After sputtering a set of samples for a series of different times, the ^{31}Si radioactivity left in the sample was determined by β measurement with a Geiger-Muller counter. Counting usually started about 8 h after the end of the neutron activation. The silicide thicknesses of the samples before and after sputtering were determined by Rutherford backscattering of 2-MeV ^4He particles.[5]

For an "in core" thermal neutron flux of 7×10^{12} n/cm^2sec, a zero count rate (normalized to a time corresponding to the end of the neutron activation) of approximately 20 cpm was obtained from 1 Å of silicon per cm^2, after a 1-h irradiation in the nuclear reactor. From the activity measurement of an unsputtered sample and from the densities of Si and Ni_2Si the thickness of the initial radioactive Ni_2Si could thus be determined. In Fig. 2 the calculated radioactive marker profile is given after initial silicide formation at the silicon substrate interface. Also shown is the activity profile after complete silicide formation (see flagged points). It is clear that the radioactive marker has moved to the surface of the sample during silicide formation and that it has also undergone some broadening. The formation of Ni_2Si thus takes place by either Ni interstitial, grain-boundary, or substitutional diffusion, or by Si substitutional diffusion (see Fig. 1). If an equally conclusive experiment can be executed with a radioactive Ni marker as well, a definite answer can be obtained regarding the diffusing species and its mechanism of diffusion. It should however be noted that even with both metal and silicon radioactive markers, one cannot distinguish between grain-boundary and interstitial diffusion. Implanted noble-gas marker experiments show that Ni is the moving species during Ni_2Si formation,[1,2] while kinetic studies show that Ni_2Si forms two times faster on ⟨100⟩ silicon than on ⟨111⟩ silicon at 275 °C because of smaller grain size.[6] The radioactive Si marker, implanted noble-gas marker, and rate dependence on grain size results are all consistent with the hypothesis that the dominant mass transport during Ni_2Si formation is grain-boundary diffusion of Ni.

Radioactive silicon used as a marker can give information about the moving species and its mechanism of diffusion during silicide formation. The sensitivity limit (amount of radioactive silicon giving a count equal to three times the standard deviation of the background count) of the technique is approximately 5 $Å/cm^2$ when activity measurement starts about 8 h after the end of the neutron activation. The background count for the Geiger-Muller detector was usually 16 cpm. The main disadvantage of the technique is that the radioactive Si is not an immobile marker and only gives a unique answer when silicon is the diffusing species. For silicides where the metal is the moving species a

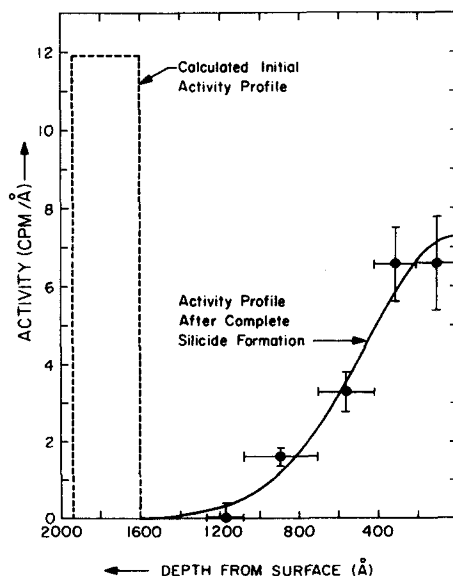

FIG. 2. Activity profile of the radioactive silicon marker (flagged points) after complete Ni_2Si formation. The radioactive marker profile after initial silicide formation at the Si ⟨100⟩ interface is also shown.

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radioactive metal marker should be used, or additional information should be obtained from other marker techniques such as implanted noble-gas markers. Also, for silicides which form at high temperature the self-diffusion of silicon in the silicide may be so large that the radioactive silicon marker may spread throughout the silicide layer, thereby losing its usefulness as a marker. The radioactive Si marker technique does, however, have the advantage that it can be applied to all silicides and that no foreign atoms are introduced into the system, thereby eliminating erroneous results from interface dragging.

The authors wish to thank Professor V. Guinn and Professor G. Miller for their advice and assistance with the neutron activation of silicon samples in the Triga nuclear reactor at the University of California, Irvine. They would also like to thank Professor D. S. Burnett of the Department of Geochmistry, California Institute of Technology, for the use of his β-counting equipment. J. Mallory is thanked for the skill and care with which he carried out the evaporations, and special thanks are due to Dr. A. Katzir, for the many hours he spent in helping the authors to carry out the sputter etching of the samples. They are also thankful to Professor J.W. Mayer of Caltech and Dr. King-Ning Tu of IBM, T.J. Watson Research Center, N.Y., for numerous fruitful discussions. One of us, R. Pretorius, thanks the South African Council for Scientific and Industrial Research for financial support.

* Work supported in part by the Office of Naval Research (L. Cooper).

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‡ Supported by Hughes Aircraft Company, Research Laboratories Division, Malibu, Calif.

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Self-aligned three-dimensional $Ga_{1-x}Al_xAs$ structures grown by molecular beam epitaxy

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(Received 30 November 1976; accepted for publication 9 March 1977)

Local thicknesses of a GaAs epitaxial layer grown on a mesa stripe by semiparallel Ga and As_4 molecular beams have been found to be proportional to $\cos\phi_{Ga}$, where ϕ_{Ga} is a local incident angle of the Ga beam to a local crystal growing surface. Submicron-thick three-dimensional GaAs-$Ga_{1-x}Al_xAs$ multilayers have been grown self-aligningly on corrugated structures with a 8-μm period. The layer thicknesses and AlAs compositions (x) are also interpreted by the local incident angles of Ga and Al beams, while evidence of atom diffusion is revealed.

PACS numbers: 68.55.+b, 81.15.Gh

It has been thought indefinitely that three-dimensional epitaxial layers can be grown by molecular beam epitaxy (MBE) without any mechanical masks.[1] To realize this presumption, it is necessary that local arrival rates of a molecular beam can be controlled, and that the surface diffusion length of adsorbed atoms be short enough compared with a length of spatial variation of local arrival rates. The latter is fulfilled for MBE of GaAs: It has been found that the surface diffusion length of adsorbed Ga on a As-stabilized (100) GaAs surface is less than 200 Å.[2] The former can be overcome by the well-known concept described below: Although only divergent beams are used for MBE, when a solid angle at an arbitrary point on the substrate surface subtended by the aperture of the beam source is small, the beam can be regarded actually as parallel for a small area of the surface. On a plane surface the beam impinges uniformly with a fixed incident angle. On the other hand, when the surface is not flat, the incident angle varies point by point on the surface; consequently, the local arrival rate is proportional to $\cos\phi$, where ϕ is the local incident angle.[3]

This paper reports that the concept described above is experimentally true for GaAs epitaxy and that three-dimensional $Ga_{1-x}Al_xAs$ epitaxial layers have been grown by a technique based on the concept.

Mesa stripes and corrugated structures with a 8-μm period parallel to the [01̄1] crystallographic direction were formed on a half major surface of (100)-oriented GaAs substrates by usual photolithographic techniques, and by preferential etching.[4] Figure 1 shows schemati-

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