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Controllable surface-plasmon resonance in engineered nanometer epitaxial silicide particles embedded in silicon

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Epitaxial $CoSi_2$ particles in a single-crystal silicon matrix are grown by molecular-beam epitaxy using a technique that allows nanometer control over particle size in three dimensions. These composite layers exhibit resonant absorption predicted by effective-medium theory. Selection of the height and diameter of disklike particles through a choice of growth conditions allows tailoring of the depolarization factor and hence of the surface-plasmon resonance energy. Resonant absorption from 0.49 to 1.04 eV (2.5 to 1.2 μm) is demonstrated and shown to agree well with values predicted by the Garnett theory using the bulk dielectric constants for $CoSi_2$ and Si.

Optical absorption due to surface-plasmon excitation in small metallic particles has been widely studied for the case of elemental metals embedded in insulating hosts such as SiO_2 or Al_2O_3,[1,2] though metals embedded in Si have also been reported.[3] Several effective-medium theories have been brought forth to describe the dielectric properties of composites, dating back more than a century.[2] Experimental results on particles of varying size and volume fraction have been successfully modeled. Accurate control of particle shape has not been possible, however, so that the theoretical dependence of plasmon energy on the depolarization factor of the particles has been difficult to verify.

We report here resonant absorption in epitaxial silicide particles embedded in a single-crystal Si matrix. Advances in fabrication technology have allowed us to control the silicide particle shape in three dimensions on a nanometer scale. This permits tailoring of the depolarization factor and hence of the plasmon resonance energy over a wide range (0.49–1.04 eV). The dependence of the resonance energies on particle shape agrees well with that predicted by the Clausius-Mossotti relation.[1] This is the first demonstration of resonant absorption in a composite material in which the metal is a silicide, and in addition, such a high degree of control over particle shape has not been available previously in any system.

Metal silicides are technologically important materials for such applications as metallization in integrated circuits, infrared detectors, and high-speed transistors. $CoSi_2$ has been heavily studied as a result of its similar crystal structure (cubic fluorite) and close lattice constant (1.2% mismatch) to those of Si. High-quality epitaxial layers have both been grown on Si substrates and overgrown with epitaxial Si.[4] The optical properties of $CoSi_2$ thin films have been measured by several workers.[5–7] In our laboratory, an infrared detector has been demonstrated recently which utilizes photoemission from electrically floating silicide particles.[8] Band-structure calculations have been carried out for $CoSi_2$,[9] and the atomic structure of the $CoSi_2$/Si(111) interface has been studied by a number of workers as a model metal-semiconductor interface. We have achieved accurate control of the microstructure of $CoSi_2$ particles embedded in a Si matrix by the use of columnar epitaxy, a technique which allows the growth of single-crystal columns of epitaxial silicides surrounded by single-crystal Si.[10]

The samples were grown in a Riber EVA320 molecular beam epitaxy (MBE) system on (111) oriented Si wafers boron doped in the 10^{15}-cm^{-3} range which were cleaned by a previously described technique.[11] Alternating Si and columnar $CoSi_2$/Si layers were then grown, with a total of three columnar layers on each sample. The Si layers were all grown at 650 °C to a thickness of 400 Å, and the columnar layers were grown at 650 °C, 700 °C, 750 °C, and 800 °C to a thickness of 100 Å. The samples will be referred to by these latter temperatures (T_{col}). In columnar epitaxy, the effect of increased substrate temperature is to increase both the silicide column diameter and the average spacing between columns. These layers were grown by codeposition of Si and Co in a 20:1 ratio from separate electron-gun evaporators. Reflection and transmission measurements were made on the samples described above, and on a bare Si wafer, using a Mattson Fourier-transform infrared spectrometer.

A plan-view transmission electron microscopy (TEM) image of the sample grown at 750 °C, and cross-sectional images of samples grown at 650 °C, 700 °C, 750 °C, and 800 °C are shown in Fig. 1. In the 800 °C sample, the particles coalesced into one layer, but TEM lattice imaging of the 800 °C particles shows the structure is similar to that of particles formed without this coalescence. All of the $CoSi_2$ particles are observed to have the type-*B* orientation, in which the silicide lattice is rotated 180° about the [111] surface normal with respect to the surrounding Si. While the Si surrounding the particles is single crystal, planar twins or stacking faults propagate through the Si from the tops of many of the particles. These faults are not expected to significantly affect the absorption properties of the composite layers.

Absorption for each of the samples was obtained from the reflection and transmission data and is shown in Fig. 2, along with the absorption from a Si substrate. Peaks in the absorption are observed (indicated by arrows) which shift with increasing growth temperature from 1.04 to 0.49 eV. In contrast, we have found that the absorption of planar $CoSi_2$ films is relatively flat over this energy range.

The absorption of the composite layers has been modeled using three-dimensional effective-medium theory. The samples actually contain two-dimensional sheets of particles, but no attempt was made to use a two-dimensional theory. In addition, the modeling treats the particles as randomly distributed in the composite layer. This is clearly not the case in the direction perpendicular to the wafer surface [as seen in Figs. 1(b)–1(e)], and may not be true in the lateral direction either, though the plan-view micograph 1(a) does not reveal obvious ordering. Finally, the effects of particle size and volume fraction are not included, as these are small compared to the effect of the widely varying depolarization factors.[12]

The original Garnett theory[13] assumes spherical metallic particles; i.e., a depolarization factor of $\frac{1}{3}$. The effect of different depolarization factors L_m has been taken into account by Cohen *et al.*,[1] who give the following relation for the dielectric constant $\epsilon_c(\omega)$ of the composite:

$$\frac{\epsilon_c(\omega)-\epsilon_i(\omega)}{L_m\epsilon_c(\omega)+(1-L_m)\epsilon_i(\omega)} = (1-x)\frac{\epsilon_m(\omega)-\epsilon_i(\omega)}{L_m\epsilon_m(\omega)+(1-L_m)\epsilon_i(\omega)}\,, \tag{1}$$

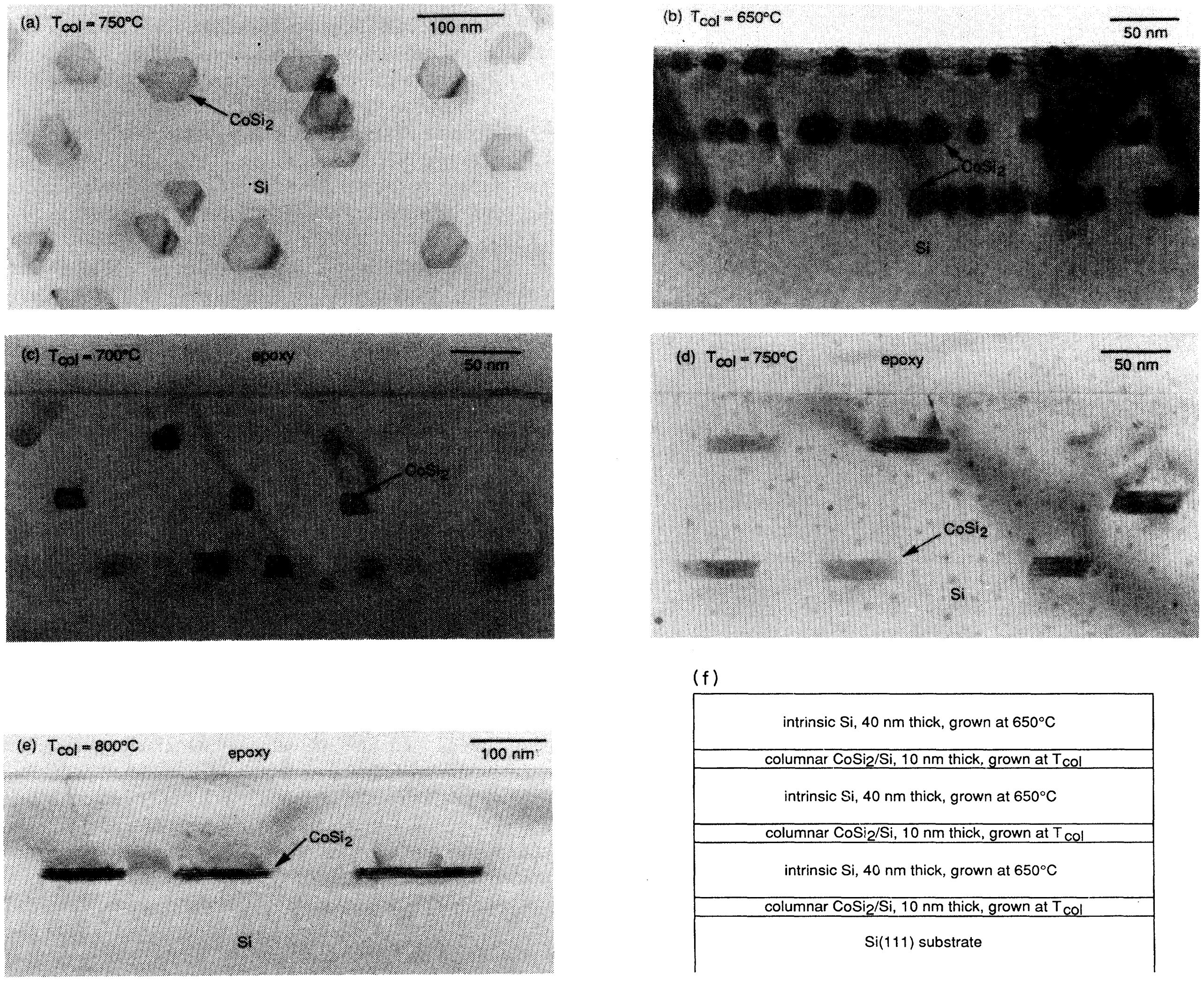

FIG. 1. (a) Plan-view TEM micrograph of the sample grown at 750 °C. (b)–(e) Cross-sectional TEM micrographs of the samples grown at 650 °C, 700 °C, 750 °C, and 800 °C, respectively. (f) Schematic diagram of the cross section of the structures. The dark regions correspond to particles of epitaxial $CoSi_2$, which are surrounded by epitaxial Si. The speckled appearance seen throughout (d) is an artifact of the sample preparation process, and the top Si layer of the 650 °C sample (b) was ion milled away during the preparation process.

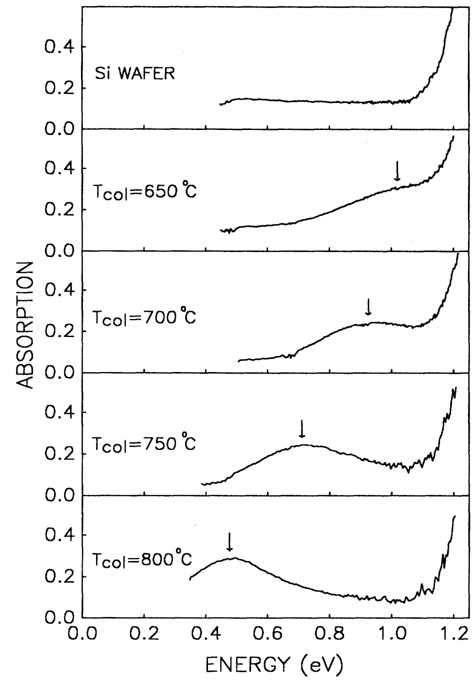

FIG. 2. Absorption spectra measured for samples with columnar layers grown at the indicated temperatures, and also for a bare Si wafer. Arrows indicate the position of peak absorption due to the composite layers.

where $\epsilon_i(\omega)$ is the insulator (Si, in this case) dielectric constant, $\epsilon_m(\omega)$ is the metal dielectric constant, and $1-x$ is the volume fraction of metal. Validity of this theory relies on the dimensions of the metallic particles being small compared to the wavelength of the radiation and on $1-x$ being less than $\approx 15\%$.

We have calculated depolarization factors for the silicide particles under the assumption that they are circular ellipsoids.[14] The actual shape is determined by crystallographic faceting, so that the cross section is approximately hexagonal, as seen in Fig. 1(a). Circular ellipsoids are mathematically tractable, however, and should serve as a reasonable approximation to the actual shape of the particles. The average aspect ratios (height to diameter) of the particles were obtained from the TEM micrographs [Figs. 1(b)–1(e)] and were used to calculate the depolarization factor of each of the samples. The values obtained for L_m (in units of 4π) are 0.39, 0.32, 0.18, and 0.11 for the samples grown at 650 °C, 700 °C, 750 °C, and 800 °C, respectively.

Absorption coefficients for the composite layers were calculated using Eq. (1) with the L_m values obtained as described above, known Si dielectric constants,[15] and $CoSi_2$ dielectric constants obtained from measurements on monocrystalline thin films.[5-7] The data of Duboz *et al.*[7] were used from 0.5 to 1.0 eV, while those of Jimenez *et al.*[5] were used form 1.05 to 1.5 eV. The epitaxial structure consisting of three columnar layers with intrinsic Si spacers is treated as a single composite layer with a metal volume fraction of 2.2%. Within each columnar layer, the metal volume fraction is $\approx 11\%$, which is still within the bounds for which Garnett theory can be successfully applied.[12] The calculated absorption coefficients show peaks corresponding to the surface plasmon energy. The position of these peaks is plotted versus growth temperature in Fig. 3 along with the experimentally observed peak positions. While the calculated peak positions occur at slightly higher energies than the observed peaks, the shifts with growth temperature agree quite well. The discrepancy in peak position is clearly systematic, and could be due to one or more of the assumptions made in the modeling.

The absorption of an entire structure, consisting of the 150-nm-thick composite layer grown at 750 °C on a Si substrate, was calculated using normal procedures,[16] with the dielectric constants obtained for the composite layer from Eq. (1). The result of this calculation is shown along with the experimental data in Fig. 4. We also carried out the calculation for a single thin composite layer capped by intrinsic Si [similar to Fig. 1(e)], and with composite layer thicknesses other than 150 nm. For all cases, the shape and position of the absorption peak were found to be approximately the same. While the theory successfully predicts the general shape and position of the experimental peak, the calculated peak is narrower and has a higher maximum value. These differences can be attributed to the fact that there is a distribution of particle diameters in the epitaxial structure, while the calculation assumes the depolarization factor is the same for all of the particles. Note that there are no adjustable parameters in the calculation.

The columnar epitaxy growth technique is not limited to $CoSi_2/Si$, and to date has been demonstrated in the

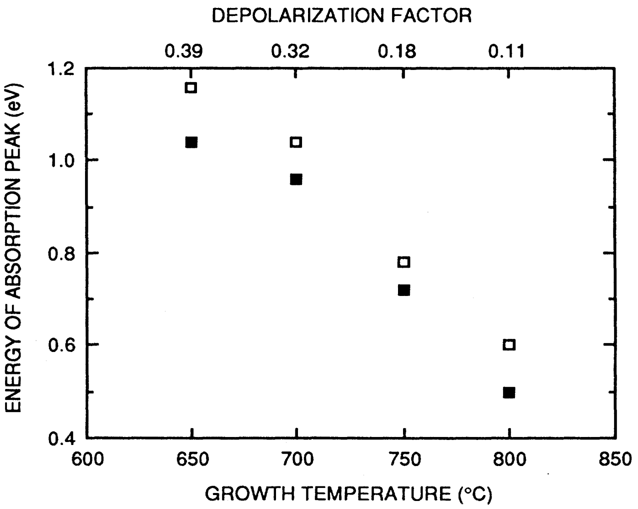

FIG. 3. Peak absorption position (from Fig. 2) vs growth temperature (solid squares), along with calculated peak positions of the absorption coefficient (open squares). The upper scale indicates the depolarization factor determined from TEM micrographs.

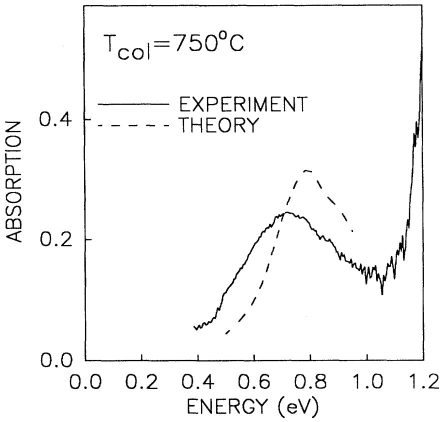

FIG. 4. Measured and calculated absorption for the full structure consisting of the 750 °C epitaxial layer on a Si substrate.

PtSi/Si (Ref. 17) and $CrSi_2$/Si (Ref. 18) systems as well. In contrast to $CoSi_2$ and PtSi, $CrSi_2$ is a semiconductor, and $CrSi_2$/Si composite layers are expected to offer very different optical properties. This family of epitaxial silicide/Si structures with nanometer control in three dimensions will allow detailed examination of optical and other physical properties of well-controlled composite media.

In summary, resonant absorption has been observed in epitaxial $CoSi_2$/Si composite materials grown by MBE. The resonance energy is controlled over the range 0.49–1.04 eV through selection of growth parameters. The position and magnitude of the resonances agree well with calculations based on Garnett theory. Future work will include fabrication of structures with smaller L_m to shift the plasmon resonance to lower energies and examination of silicides other than $CoSi_2$.

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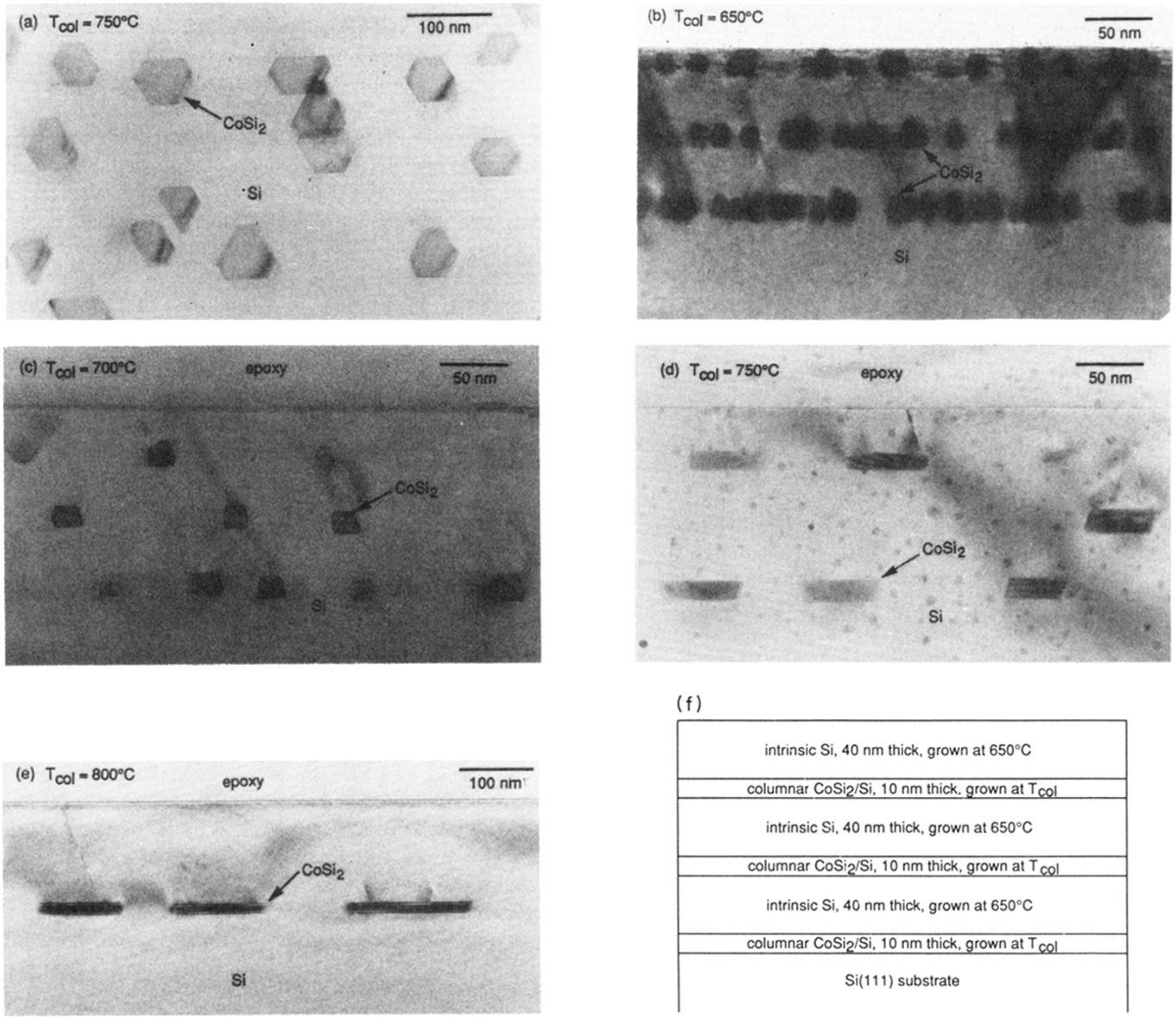

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