Raman microprobe analysis of tungsten silicide
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A$_{0.47}$In$_{0.53}$As-Ga$_{0.47}$In$_{0.53}$As APD's. A positive hysteresis appears for $V_{PT} < V_R < 28$ V, and a reversible decrease in the luminescence efficiency of the Ga$_{0.47}$In$_{0.53}$As layer is observed when $V_R \rightarrow 0$ V. This indicates that when the electric field sweeps the layer, nonradiative recombination centers are formed in the InGaAs. These centers reduce the luminescence efficiency and also modify the charge density in the space-charge region and consequently the punchthrough voltage. One possibility is that these centers could result from a defect reaction assisted by the electric field. The positive shift of $V_{PT}$ indicates that compensating acceptorlike centers are introduced with a concentration of $\approx 5 \times 10^{15}$ cm$^{-3}$. These experiments show that the presence of an electric field at a heterointerface modifies the minority-carrier distribution and affects considerably the cathodoluminescence properties of the epitaxial layers in a manner similar to that reported for bulk materials. By this technique, the position of the interface is obtained in good agreement with C-V profiles, and the observation of hysteresis in the CL quenching curve is related to deep centers near the interfaces. Moreover, the punchthrough voltage can be locally estimated, and as $V_{PT}$ is directly related to the doping, local dopants and/or electric field fluctuations can be measured as demonstrated in a study of microplasmas. In addition to providing an in-depth resolution of radiative and nonradiative processes at an interface, this technique allows the formation of spatially resolved maps of radiative centers and deep traps at heterostructure interfaces.

Raman microprobe analysis of tungsten silicide

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The Raman spectrum of tungsten silicide has been observed and is reported for the first time. It was obtained on the MOLE$^{10}$ Raman microprobe during the examination of an annealed sample of tungsten deposited over crystalline silicon. A similar examination of fine tungsten lines, 8 $\mu$m wide by 20 nm thick, selectively deposited on a crystalline silicon surface using laser-induced chemical vapor deposition techniques, produced an identical spectrum superimposed with that of the silicon substrate. This observation demonstrates the capability of the Raman microprobe to analyze the formation of solid silicide phases on a microscopic scale. The technique offers a rapid and nondestructive method for the identification of tungsten silicide either in the bulk or as a component in an integrated circuit.

Refractory metal silicides are expected to play a vital role in the development of very large scale integration (VLSI) technology. They have therefore been the topic of numerous investigations regarding both their preparation and characteristics. The results of these investigations have been summarized in review articles.$^{1,2}$ Several of these articles report the most promising materials to be WSi$_2$, MoSi$_2$, TaSi$_2$, and TiSi$_2$. Additional silicides, NbSi$_2$, PtSi, and PdSi, have also been studied. In the case of the last two materials, the studies have included the observation of Raman spectra of silicides with several different stoichiometric ratios. Most of the early studies were done using interference-enhanced Raman scat-
tering, which enhances the intensity of the radiation in the interface between the metal and the substrate. A recent study reported the detection of PtSi without the use of a special sample geometry for signal enhancement. The Raman spectra obtained in these studies were used to identify the silicide and gauge the apparent crystallinity of the material. Raman data on the remaining silicides have been conspicuously absent from the published literature.

The aim of the Raman microprobe study reported here was to analyze the composition and structure of the material produced during the deposition of a tungsten line pattern on crystalline silicon. The refractory metal lines were prepared by selective chemical vapor deposition using tungsten hexafluoride. A silicon sample freshly cleaned in a HF solution was placed in a reaction chamber containing about 50 Torr tungsten hexafluoride at room temperature. An argon-ion laser operated at 8–10 W was focused onto the sample surface and scanned at a speed of about 5 cm/s. The chemical pathway for tungsten deposition was initiated by the surface reduction of gas phase tungsten hexafluoride at the silicon surface temperature of about 350°C. Higher temperature leads to the formation of tungsten silicides.

An Auger analysis of the lines, each having a width of approximately 8 μm and a depth of 200 Å, revealed that they contained tungsten and silicon. However, the form, or phase, of the material could not be determined from the Auger data. This left a very important question unanswered. Is the film a form of silicide, or is the silicon dissolved in the tungsten? The search for a resolution of these questions led to the Raman microprobe examination of the deposited material. Initially, a Raman spectrum of a known tungsten silicide on silicon film was obtained as a reference spectrum. The sample was also examined by x-ray diffraction. The diffraction pattern was found to correspond to the published data for WSi₂, Joint Committee on Powder Diffraction Standards card No. 11-195.

The Raman spectra were recorded on a MOLE® Raman microprobe based on a Ramanor U-1000 double-grating spectrometer with a microscope attachment. The sample was excited with the 514.5-nm emission of an argon-ion laser. The light was focused to a 1-μm spot using laser powers between 30 and 70 mW. The laser power at the sample was approximately an order of magnitude less. The scattered light was imaged on the spectrometer entrance slit. All samples were examined without preparation.

The Raman spectrum of the tungsten silicide reference sample is shown in Fig. 1. The spectrum exhibits two peaks. The first at 331 cm⁻¹ is fairly sharp, whereas the second, at 451 cm⁻¹, is broad. The small band at 520 cm⁻¹ is due to crystalline silicon. This band probably originates from small regions of crystalline silicon in the tungsten silicide, since the 0.2-μm depth of the silicide is sufficient to block any emissions from the substrate. This statement is also consistent with the observation that the stoichiometric ratio, as determined by RBS and Auger, is slightly larger than the anticipated value of 2. Several spectra of this sample were produced with laser power settings between 30 and 70 mW. The spectra were identical, and no spectral discontinuities usually associated with sample degradation were observed. In addition, visual inspections after prolonged laser examination revealed no signs of sample damage.

The Raman spectrum of a small area of one of the deposited lines is shown in Fig. 2. Both Raman peaks at 331 and 451 cm⁻¹, identical to those of the annealed tungsten over silicon film, are plainly visible, as is the very intense Raman peak at 521 cm⁻¹ due to crystalline silicon. This clearly implies that the material in the line is tungsten silicide. The large crystalline silicon line is probably observed because the 20-nm-thick film of the silicide is inadequate to attenuate the irradiation to and from the underlying silicon. Similar Raman spectra were obtained from several areas

FIG. 1. Raman spectrum of tungsten silicide obtained from an annealed tungsten oxide on a crystalline silicon substrate. Enlargements shows that the small line at 520 cm⁻¹ is due to crystalline silicon in the tungsten silicide. Spectrum is the summation of five scans with points spaced by one wave number and an integration time of 10 s/point.

FIG. 2. Representative Raman spectra of material located in an 8-μm tungsten line deposited on a crystalline silicon substrate. Large band at 521 cm⁻¹ is due to the substrate. Spectrum is the summation of two scans with points spaced by one wave number and an integration time of 4 s/point.
Carrier lifetime model for the optical degradation of amorphous silicon solar cells

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The light-induced performance degradation of amorphous silicon solar cells is described well by a model in which the carrier lifetimes are determined by the dangling bond density. Degradation will be slower in solar cells operating at lower excess carrier concentrations. This is documented with a comparison of degradation data for cells at open circuit versus load, and for single versus cascade cells. At sufficiently long times, the efficiency will decrease at approximately the same rate for all cases, with an offset in time between the individual cases which can be calculated.

When hydrogenated amorphous silicon (a-Si:H) solar cells are exposed to light, their performance characteristics degrade with time. The mechanism of this degradation is usually assumed to be related to the light-induced changes in photoconductivity in a-Si:H known as the Staebler–Wronski effect, a result of the increase in the density of dangling bonds, \( N_d \), to the intensity and duration of exposure. They proposed a kinetic model in which the carrier lifetime is limited by recombination centers in the gap associated with the dangling bonds, and dangling bonds are generated by a band-to-band recombination process. If the temperature is sufficiently low that annealing effects can be neglected, the rate constant for band-to-band transitions, where \( r_i \) is the rate constant for band-to-band transitions,

\[
\frac{dN_d}{dt} = c_{sw} r_i np,
\]

\( c_{sw} \) is the density of unpaired spins associated with dangling bonds, \( N_d \), to the intensity and duration of exposure. They proposed a kinetic model in which the carrier lifetime is limited by recombination centers in the gap associated with the dangling bonds, and dangling bonds are generated by a band-to-band recombination process. If the temperature is sufficiently low that annealing effects can be neglected,

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