A semiconductor sensor adapted to detect with a high degree of sensitivity small magnitudes of a mechanical force, presence of traces of a gas or light. The sensor includes a high energy gap (i.e., \( \sim 1.0 \) electron volts) semiconductor wafer. Mechanical force is measured by employing a non-centrosymmetric material for the semiconductor. Distortion of the semiconductor by the force creates a contact potential difference (cpd) at the semiconductor surface, and this cpd is determined to give a measure of the force. When such a semiconductor is subjected to illumination with an energy less than the energy gap of the semiconductors, such illumination also creates a cpd at the surface. Detection of this cpd is employed to sense the illumination itself or, in a variation of the system, to detect a gas. When either a gas or light is to be detected and a crystal of a non-centrosymmetric material is employed, the presence of gas or light, in appropriate circumstances, results in a strain within the crystal which distorts the same and the distortion provides a mechanism for qualitative and quantitative evaluation of the gas or the light, as the case may be.

11 Claims, 8 Drawing Figures
FIG. 3

XENON LAMP - MONOCHROMATOR - CHOPPER - SCREEN

LASER

VACUUM PUMP

FIG. 4B

BENDING

UNBENDING

2.5 min

time

FIG. 4D

SURFACE STRAIN (1.3.10⁻⁴)

V₆⁰ = -1.6 volt

V₆⁰ = -1.5 volt

V₆⁰ = -0.9 volt

V₆⁰ = -0.85 volt

(00.1)

(00.1)
SEMICONDUCTOR SENSORS

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 U.S.C. 2457).

This is a continuation of application Ser. No. 492,118, filed July 26, 1974 (now abandoned), which was a division of application Ser. No. 290,666, filed Sept. 21, 1972 (now U.S. Pat. No. 3,887,937, granted June 9, 1975).

The present invention relates to sensors and, in particular, to semiconductor sensors that are useful to detect very small values of mechanical force, traces of a gas or light.


Surface photovoltage spectroscopy, which is in the term used by the present inventors to described their method of studying electron configurations on semiconductor surfaces, is based on the photostimulated de-population and population of surface states brought about by sub-bandgap (i.e., an energy less than the energy gap of the semiconductors) monochromatic illumination, while the overall number of bulk free carriers remains essentially unchanged. Such transitions and their transients (as determined by changes in the contact potential difference) allow the direct determination of the energy positions and the dynamic parameters of the surface states. Surface photovoltage spectroscopy has been successfully applied by the present inventors to the surfaces of CdS, ZnO and GaAs, high energy gap semiconductors.

The photovoltaic effect, i.e., the appearance of a voltage upon illuminating a semiconductor-metal rectifier, was reported nearly one hundred years ago. However, it was not until 1948 that this effect was employed to study semiconductor surfaces, primarily through band-to-band transitions leading to the generation of free carriers. In this type of experiment, the role of surface states was studied through the trapping and recombination of excess carriers. The present inventors have observed surface photovoltage in the above materials under sub-bandgap illumination, where apparently no band-to-band transitions are involved. Under such sub-bandgap illumination, the surface photovoltage is associated with discrete electron transitions from the surface states into the conduction band and from the valence band into the surface states.

In the case of non-centrosymmetric (piezoelectric) high energy gap semiconductor compounds, a stress applied through mechanical bending of thin wafers corresponds to an applied electric field which causes an increase or decrease in the surface barrier height depending on the direction of bending (surface piezoelectric effect). In the latter case it has been shown that equilibrium is established between the surface states and the bulk. Thus, it is now possible, by combining controlled mechanical bending (and unbending) and surface photovoltage spectroscopy, to study the characteristics of the surface states under equilibrium conditions. It is also possible to relate the surface states to the magnitude of the mechanical bending force, thereby to supply a mechanism for determining that force. Accordingly, a principal object of the present invention is to provide a semiconductor device suitable for use as a mechanical force sensor.

When the semiconductor is placed in a vacuum and traces of a gas are introduced into the system, the condition of the surface states is modified and the gas can be sensed thereby. A further object, therefore, is to provide a semiconductor gas sensor.

The high energy gap semiconductor if subjected to light exhibits a contact potential difference which is a function of the amount of radiation and the frequency thereof. Furthermore, if the semiconductor is non-centrosymmetric, it undergoes strain, that is, elastic deformation or mechanical vibrations. Either phenomenon can be noted. It is another object, therefore, to provide a sensing system to detect the presence of light and to indicate the frequency of the light.

These and other objects are found in the description that follows and are particularly pointed out in the appended claims.

The objects of the invention are embodied in a sensing system that includes a high energy-gap semiconductor wafer. Means is provided to effect changes of population of the surface states of the semiconductor thereby to effect changes in the surface barrier without affecting the bulk carrier concentration in the bulk material. There is also provided means for detecting the changes in the surface states as a consequence of said changes in population and for relating the same to the thing to-be-sensed.

The invention will now be discussed with reference to the accompanying drawing in which:

FIG. 1 is a schematic of a semiconductor sensing system of the present invention, partially block diagram in form;

FIG. 2 is a schematic representation of the surface states of the prismatic surfaces of a CdS semiconductor and the associated electron transitions;

FIG. 3 shows a part of a system which is a modification of the system of FIG. 1 and shows a CdS wafer secured at one end thereof and subjected to deformation by changes effected in the surface states of the crystal;

FIG. 4A is a schematic representation of a part of a system that is a modification of the system of FIG. 1 and is intended to relate bending of a non-centrosymmetric crystal and contact potential difference (cpd);
FIG. 4B is a graph of contact potential difference as a function of bending and unbending of the crystal shown in FIG. 4A. FIG. 4C shows the orientation of the crystal of FIG. 4A; FIG. 4D relates changes in cpd to the radius of bending and surface strain; and FIG. 5 illustrates the crystallographic orientation of the semiconductor wafer of FIGS. 3 and 4.

Turning now to the drawing a sensor or sensing system of the present invention is shown at 101. The system 101 comprises a high energy-gap semiconductor wafer 1 which may be made, for example, of CdS, ZnO or GaAs. As used herein "high" denotes a semiconductor having a gap ~1.0 eV or higher at room temperature; operation at lower than room temperatures allows use of proportionately lower energy-gap materials. Such other materials can be employed within the present teachings and the gap thereof is considered "high" in the context of this specification. The sensing system 101 can be employed to measure an occurrence which affects changes in the population of the surface states of the semiconductor wafer, to effect changes in the surface barrier but without appreciably affecting the electrical carrier concentration in the bulk material thereof. Such an occurrence can be a force resulting in a bending moment upon the wafer 1, which results in a contact potential difference (cpd) at the wafer surface; or the occurrence can be the presence of the photons again resulting in a cpd; or the occurrence can be the presence of a gas in a vacuum environment which results in changes in cpd otherwise effected — all as discussed in detail hereinafter. Thus, all these phenomena can be detected by voltage sensing means, but, as is explained in later paragraphs, the latter two can be sensed by noting deformation of the wafer due to the said population changes.

The cpd is measured by voltage sensing means which, includes essentially most of the circuit elements in FIG. 1, as now explained. (The explanation given here is taken to a large measure from the article entitled, "Electronic Characteristics of 'Real' CdS Surfaces", which can be referred to for amplification of the present disclosure.) The voltage sensing circuitry includes a gold-base reference electrode or probe which can be referred to for amplification of the pre-amp circuit in FIG. 1, as later discussed. First, however, there

elsewhere herein it is mentioned that changes in the population of the surface states can be effected by illuminating the semiconductor crystal but that, in the case of non-centrosymmetric crystals, that same change can be effected by application of a mechanical bending force upon the crystal. The latter effect is now discussed with reference to FIG. 4A wherein the semiconductor crystal is designated 1B. A sensing circuit like the circuit in FIG. 1 can be employed. In work done, a surface piezoelectric effect was found whereby mechanical bending of CdS wafers with an (00.1) orientation caused pronounced changes (of the order of one volt) in the contact potential difference. This effect was attributed to the polarization induced in the depletion layer by the mechanical stress. The wafer 1B employed measured 13 X 3 X 0.08 mm. It was cut from a high purity, n-type single crystal with a resistivity of about 2 ohm-cm, mechanically ground, polished with an 0.25 μm particle size abrasive. It was chemically etched (in 0.5 N K₂Cr₂O₇:16 N H₂SO₄) to the final dimensions to remove all surface damage introduced during polishing. Ohmic contacts were made employing indium in a hydrogen atmosphere. Contact poten-
where \( c^e \) is the elastic stiffness; its value calculated for the present bending configuration is \( 5.6 \times 10^{10} \text{ N/m}^2 \).

A macroscopic manifestation of the polarization in eq. (1) is not possible in the bulk since the carrier concentration is high \( (n_p=10^{19} \text{cm}^{-3}) \) and their redistribution shortens out the polarization. However, in the depleted surface region where the free carrier concentration is essentially zero, polarization \( P_3 \) can be readily manifested macroscopically. Assuming that, upon bending (at time \( t=0^- \)), the observed changes in cpd at \( t=0^+ \) are not shielded by the surface states and that a Schottky-type surface barrier is present, then it can be shown that the system at hand can be described by the following set of one-dimensional equations:

\[
P_0 = P_0 + \varepsilon_0 E_0.
\]

\[
\Delta D_b | \text{surface} = Q_{sw}.
\]

where \( \Delta D_b \) is electric displacement; \( \varepsilon \) is the dielectric constant; \( \varepsilon_0 \) is the permittivity of free space; \( E_0 \) is the electric field; \( \rho \) is the charge density; \( V \) is the potential barrier; \( Q_{sw} \) is the surface state charge density. For \( V_3 = V_{30}^0 + \Delta V_3 \), \( \Delta V_3 < - kT/q\) (Schottky-type surface barrier), it follows from the above set of equations (for \( t=0^+ \)):

\[
|V_3| + \Delta V_3|_{t=0} = |V_3|_{t=0^+} = |V_3| + \Delta V_3 = |V_3|_{t=0^+} + \Delta V_3.
\]

where \( \Delta V_3 \) is linearly related to the change in bulk and \( \varepsilon_0 \) is the strain at the surface. Introducing a measurable quantity \( Z \) defined as

\[
Z = |d\Delta V_3/d\varepsilon_s|_{t=0^+} = \text{there is obtained from eq. (6) (the following expression:}
\]

\[
Z = \frac{4\pi e_0}{c^e} |V_3 + \Delta V_3|.
\]

According to eq. (7), \( Z^2 \) is linearly related to \( \Delta V_3 \), i.e., the cpd upon bending (\( t=0^+ \)). Experimental results bear out this relationship. It will be appreciated on the basis of the foregoing discussion that very small magnitudes of force can be sensed by employing the sensor herein disclosed.

An a-c displacement signal can also be generated if the wafer-reference electrode 5 capacitance is maintained in a constant (non-vibrating) configuration and the cpd is varied periodically, as is previously noted. The periodic variation in cpd can be produced by chopped incident light. The a-c signal properly (Fouier) analyzed can serve for determining and continuously recording a-c surface photovoltage. The sample-reference electrode configuration shown in FIG. 1 can be employed as can, also, the cpd-measuring circuit. The chopping is effected by the light chopper 4, as mentioned, which is provided with its own input reference signal. In one experiment, the light incident on the wafer 1 was maintained at \( 3 \times 10^{10} \text{ photons km}^2 \). Observed surface states in the prismatic surfaces of CdS under atmospheric pressure and corresponding photo-stimulated transitions, are given in Table 1.
The surface states are shown schematically in FIG. 2.

From the above explanation it can be seen that the cpd varies as some function of intensity of incident light upon the wafer 1. It also varies as a function of the wavelength of the incident light. Thus, cpd can be employed to sense impinging radiation itself. Furthermore, if the wafer 1 is enclosed within a vacuum chamber, represented by block designation 11 in FIG. 3, and subjected to a high vacuum (~10^-11 torr), the cpd can be employed to sense very small magnitudes of a gas with which the wafer 11 can be vacuum sealed. For example, the chamber 11 is of a size and shape such that the wafer, inserted therein, is free to vibrate. In this situation the thin CdS wafer 11 exhibits pronounced bending when illuminated with white light. Chopped white light can be employed to excite the wafer to its natural frequency. However, the amplitude of vibration has been found to be a function of the frequency of the incident radiation. Thus, the embodiment of FIG. 3 can be used to detect radiation frequency in and around the visible spectrum or the presence of gases when light of a known frequency is used. Some experimental work is discussed in the next several paragraphs. The wafer being made of CdS, GaAs or other such semiconductors in work discussed in connection with FIGS. 3 and 5. It should be preliminarily noted that two parameters can be measured to give a measurable indication of the thing to-be-sensed. First, the cpd can be sensed employing an arrangement similar to FIG. 1 and, second, mechanical vibration of the wafer can be sensed employing the weak light beam shown schematically at 17 and a pick-up mechanism 18; the latter can be merely a movie-type screen.

The wafer 1, employed in the arrangement depicted by FIG. 3, measured about 10 x 3 x 0.015 mm. They were cut from carefully selected high-purity n-type CdS single crystals with a resistivity of about 1 Ohm cm. They were mechanically ground and then were chemically etched in 0.5N kCr2O7: 16N H2SO4 to their final dimensions. They exhibited initial "spontaneous bending" consistent with previously noted results on wafers of III-V compounds. The illumination arrangement consisted of a xenon lamp, a double prism monochromator and a variable frequency chopper. Typically, 10^10 photon/sec. (hν = 2.5 eV) were used to excite the wafers to their fundamental frequency vibration, which was of the order of 100 Hz. The resulting relative amplitude (amplitude divided by the length of the sample) of the vibration was of the order of 5 x 10^-2. The amplitude was determined by means of a collimated laser beam 17 reflected from the CdS wafers upon the screen 18. The intensity of the cw laser beam (λ = 0.63 μm) was reduced to a level that did not affect the bending of the wafers under study. Background illumination had to be excluded. Surface photovoltage was also measured as the light-induced change in the contact potential difference by employing a gold reference electrode 5, as before.

The spectrum of the amplitude of vibration as a function of the wavelength of the incident radiation exhibited by the CdS wafers is very similar to their surface-photovoltage spectrum and differs considerably from their photoconductivity spectrum. Accordingly, it is concluded that the observed photomechanical effect is a surface effect associated with the light-induced changes in the electric field at the surface (surface barrier). In view of the piezoelectric properties of CdS, the electric field can be related to the resulting strain on the basis of the converse piezoelectric effect. Thus, to explain the observed photomechanical effect, a model is proposed involving (a) a surface-photovoltage step and (b) an electromechanical step. Step (a) has been discussed previously herein and analyzed for CdS surfaces. Regarding step (b) in a matrix notation the electric field E⊥ in FIG. 5 is related to the strain components εij by

\[ \varepsilon_{ij} = d_{ij}E_{\perp} \]  

wherein d_{ij} is piezoelectric coefficient. For the wurtzite structure the (d_{ij}) matrix is

\[ (d_{ij}) = \begin{pmatrix} 0 & d_{ij} & d_{ij} & \cdots \\ d_{ij} & 0 & d_{ij} & \cdots \\ d_{ij} & d_{ij} & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \]
This effect can also serve as the basis for the photogen-
light beam incident on the wafer and reflected thereby onto a screen whereby the amplitude of vibration of said wafer can be measured.

6. A sensor according to claim 1 wherein said source produces steady state monochromatic illumination of said wafer.

7. A sensor according to claim 6 wherein said means for measuring the deflection of said wafer includes a vibrating probe for detecting the contact potential difference that arises due to changes in surface states in response to illumination of said wafer.

8. A sensor according to claim 1 wherein the material of the wafer has a structure like zinc-blende.

9. A sensor according to claim 4 wherein the material of the wafer has a structure like wurtzite.

10. A sensor according to claim 1 wherein the gas is oxygen and the wafer material is cadmium sulfide.

11. A method for detecting traces of oxygen in a vacuum chamber comprising the steps of:
   a. placing a cadmium sulfide wafer in the vacuum chamber;
   b. illuminating the wafer with radiation whose energy corresponds to the energy of surface states introduced by oxygen for causing the wafer to deflect an amount dependent on the wavelength of the illumination; and
   c. measuring the deflection of the wafer when it is known that oxygen is absent from the chamber so that changes in the deflection due to the presence of oxygen can be detected.

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