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Strain-induced photoconductivity in thin films of Co doped amorphous carbon

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Traditionally, strain effect was mainly considered in the materials with periodic lattice structure, and was thought to be very weak in amorphous semiconductors. Here, we investigate the effects of strain in films of cobalt-doped amorphous carbon (Co-C) grown on 0.7PbMg1/3Nb2/3O3-0.3PbTiO3 (PMN-PT) substrates. The electric transport properties of the Co-C films were effectively modulated by the piezoelectric substrates. Moreover, we observed, for the first time, strain-induced photoconductivity in such an amorphous semiconductor. Without strain, no photoconductivity was observed. When subjected to strain, the Co-C films exhibited significant photoconductivity under illumination by a 532-nm monochromatic light. A strain-modified photoconductivity theory was developed to elucidate the possible mechanism of this remarkable phenomenon. The good agreement between the theoretical and experimental results indicates that strain-induced photoconductivity may derive from modulation of the band structure via the strain effect.

Amorphous carbon (a-C) films have attracted widespread attention for use in various device applications due to their remarkable electrical, magnetic and optical properties. The variability of these physical properties is directly correlated with the films' unique dual nanostructure in which sp2-hybridized nanoclusters are embedded in the sp3-hybridized matrix. Different deposition techniques and growing conditions can be used to control the sp2/sp3 ratio, and thus modulate the characteristics of a-C films. Another method, which is expected to induce interesting physical properties, is to form a more complicated structure that includes metallic nanoparticles surrounded by the a-C matrix. By choosing the type and size of these metallic nanoparticles, researchers can design a special a-C film with the desired magnetic and optoelectronic properties. Co and Ni have been found to form spontaneously as crystalline nanoparticles in a-C films, and considerable research effort has thus been devoted to the interplay between Co or Ni nanoparticles and their effect on various optoelectronic properties.

The effects of strain have to date been investigated primarily in materials with a periodic lattice structure, and are thought to be very weak for amorphous materials. However, the recent computational results demonstrated that the piezoresistive effect of a-C films could be strengthened by embedding crystalline nanoparticles into the carbon matrix. Furthermore, the external strain might affect the optical gaps, and thus modulated their optoelectronic properties. It is interesting to study the relationship between increased strain and the optoelectronic properties in a-C films. Until now the related experimental and theoretical research still remains lacking.

Here, thin films of cobalt-doped amorphous carbon (Co-C) were grown on 0.7PbMg1/3Nb2/3O3-0.3PbTiO3 (PMN-PT) substrates. Co-doping was expected to enhance the films' sensitivity to strain. We then investigated the piezoresistive effect in these thin Co-C films. Piezoelectric PMN-PT substrates were used to strain the films reversibly, and strain was observed to induce photoconductivity. To explain such a remarkable phenomenon, a theoretical model has been developed. This basic model assumes that the band gap can be tuned via strain, thereby inducing photoconductivity from nothing. In addition to Co-C films, the model can be applied to other amorphous material systems.

The resistance of the Co-C film was measured using the four-probe method. The inset in Fig. 1a shows a schematic illustration of the electrical measurement. The bias electric field was applied across the Co-C/PMN-PT structure, and a resistor of 20 MΩ was connected in series with the PMN-PT substrate to protect the electrical meters in case there was a dielectric breakdown in the PMN-PT crystal. The leakage current was confirmed to be less than 10 nA under bias voltage of 500 V. Fig. 1a presents the hysteresis loop of resistance, with the electric field cycling from −500 V to +500 V. Here, we define ΔR/R = (R(V) − R(0))/R(0), where R(V) and R(0) are the resistances of the Co-C film with and without the bias electric field, respectively. For the forward bias, the resistance increases as the positive voltage increases and reaches its maximum value (about 40%). For the reverse bias, it decreases with an increase in the negative voltage and reaches its minimum value (about −20%). This
phenomenon cannot be explained by the strain effect alone. The shuttle-like loop of the relative change in resistance indicates that the polarization effect is dominant in resistance modulation. Major carriers in Co-C film are known to be holes. When a positive electric field is applied to a PMN-PT substrate ($V_{0}$), the electric-dipole moments will point upward into the Co-C film. The accumulation of localized negative charges in the interface between the Co-C film and the PMN-PT substrate may trap free holes in the film, thereby causing the depletion of free holes and, in turn, increasing the resistance. In the case of applying a negative electric field ($V_{0}$), the reverse effect may occur, with a decrease in resistance.

It is interesting to note that under illumination of 50 mW/cm$^2$ resistance hysteresis of the Co-C film changes from a shuttle-like loop to the butterfly-like loop shown in Fig. 1b, which implies that the strain effect rather than the polarization effect plays a dominant role in modulating the resistance. A possible explanation is as follows. In darkness, the number of localized electric charges in the interface between the Co-C film and the PMN-PT substrate may trap free holes in the film, thereby causing the depletion of free holes and, in turn, increasing the resistance. In the case of applying a negative electric field ($V < 0$), the reverse effect may occur, with a decrease in resistance.

XRD measurements were used to investigate the response of the out-of-plane lattice constant $c$ of PMN-PT (001) crystal under the applied electric field. In Fig. 1c, $c$ exhibits a hysteresis behavior in a cycle of bias voltages. Considering that the stress tends to be transferred from the PMN-PT substrate to the Co-C film, observed resistance hysteresis may derive from ferroelectric hysteresis of the PMN-PT substrate. In addition, it is found that resistance hysteresis under illumination is more pronounced than that in darkness. In order to explain this phenomenon, the sample’s conductivity can be expressed as $\sigma = \sigma_{\text{dark}} + \Delta \sigma_{\text{light}}$, where $\sigma_{\text{dark}}$ is conductivity in darkness and $\Delta \sigma_{\text{light}}$ is conductivity increase induced by the incident light. $\sigma_{\text{dark}}$ depends mainly on the charge polarization on the surface of the PMN-PT substrate, whereas $\Delta \sigma_{\text{light}}$ is a function of strain. In darkness, with $\sigma = \sigma_{\text{dark}}$, resistance hysteresis of the sample may be attributed only to hysteresis of the charge polarization. Under illumination, with $\sigma = \sigma_{\text{dark}} + \Delta \sigma_{\text{light}}$, the observed resistance is determined by the coaction of polarization and strain effects. The resistance hysteresis may be due to the sum of polarization and strain hystereses, thus being more pronounced than that in darkness.

Fig. 1d illustrates the resistance responses in a cycle of voltages ($0 \rightarrow 500 \rightarrow -500 \rightarrow 0$) in darkness and under illumination. It should be pointed out that no significant photoconductivity was observed when the bias voltage was close to zero. It is thought that in this case, the Co-C film is no longer subject to the influence of the strain effect. This result is consistent with our previous observation that a-C films are insensitive to light because of their disordered structure. However, when the bias voltage is increased, a large degree of photoconductivity can
be observed. At a bias voltage of 500 V, the resistance in darkness is almost three times larger than that under illumination. It seems that strain induces photoconductivity from nothing. Based on the strain effect, we constructed a modified model of photoconductivity in amorphous semiconductors to explain this remarkable phenomenon. Our model shows that the increase in strain can compress the band gap and thus enhance the photoconductivity effect.

Amorphous semiconductors are known to have a lattice structure with long-range disorder. It is impossible to study their transport properties on the basis of such a disordered lattice structure. An alternative means of doing so is to make use of the Fermi-Dirac distribution function in these semiconductors. The band structure of amorphous semiconductors was elucidated by Mott et al., as shown in Fig. 2. The conduction or valence band has a tail of limited depth owing to the long-range disorder. M and N discrete states are distributed at E_i and E_j, respectively, which are thought to depend on the medium-range order. In the case of Co-C films, these states may be influenced primarily by Co-doping.

Based on the band structure of amorphous semiconductors, Simmons and Taylor developed a theory of photoconductivity containing discrete trap levels. To simplify the problem, the basic model contains two trap levels: one in the upper half of the band gap (E_{tp}) and the other in the lower half (E_{tn}), as shown in Fig. 2a. In accordance with the Co-C film being of p-type, the Fermi level (E_F) is situated in the lower half. E_{tp} is initialized near the Fermi level, and E_{tn} near the reflected position of E_F with respect to the center of the band gap.

The generation rate of the electron-hole pairs can be written as:

\[
G = \frac{np}{n+p} \gamma X^\nu \left\{ \sum_{i=1}^{N} \frac{1}{1 + \exp \frac{E_{tp} - E_i}{kT}} + \sum_{j=1}^{M} \frac{1}{1 + \exp \frac{E_{tn} - E_j}{kT}} \right\},
\]

where \( n \) and \( p \) are the concentrations of the free electrons and holes, respectively, \( \rho \) is the concentration of the trap levels, \( \nu \) is the capture cross-sections of the electrons or holes for the trap, \( v \) is the thermal velocity and \( k \) is the Boltzmann constant. Under steady-state conditions, \( G \) is mainly dependent on the difference between \( E_{tp} \) (or \( E_{tn} \)) and \( E_i \) (or \( E_j \)). However, equation (1) cannot be used to analyze the strain-induced photoconductivity of Co-C films because of its irrelevance to the strain term. To solve this problem, we assume that the band gap decreases as a function of increasing strain. During this process, the compressed band gap may cause \( E_{tp} \) (or \( E_{tn} \)) and \( E_i \) (or \( E_j \)) to shift toward each other as shown in Fig. 2. The net effect is that the difference between \( E_{tp} \) (or \( E_{tn} \)) and \( E_i \) (or \( E_j \)) decreases as strain increases. Therefore, the strain term may be considered as:

\[
E_{tp}(s) - E_{tn}(s) = \Delta E_t - \gamma_p s, \quad E_i(s) - E_{tn}(s) = \Delta E_j - \gamma_n s,
\]

where \( \Delta E_t \) and \( \Delta E_j \) are determined by \( E_{tp}(0) - E_i(0) \) and \( E_{tn}(0) - E_{tn}(0) \), respectively, \( \gamma_p \) and \( \gamma_n \) are named as strain-modified sensitivities depending on the material characteristics and \( s \) is the strain coefficient. Here, to simplify the problem we assume that \( E_{tp}(s) - E_{tn}(s) \) and \( E_i(s) - E_{tn}(s) \) are both linear with \( s \). Our simulation results showed this assumption to be reasonable in Co-C film. In other amorphous semiconductor systems, the relation between \( E_{tp}(s) - E_{tn}(s) \) [or \( E_i(s) - E_{tn}(s) \)] and \( s \) can always be calculated from experimental data. From equations (1) and (2), the strain-modified equation for the generation rate \( G \) of electron-hole pairs may be written as:

\[
G = \frac{np}{n+p} \gamma X^\nu \left\{ \frac{1}{1 + \exp \frac{\Delta E_t - \gamma_p s}{kT}} + \frac{1}{1 + \exp \frac{\Delta E_j - \gamma_n s}{kT}} \right\}.
\]

Equation (3) allows us to build a bridge connecting rate \( G \) and strain \( s \).

The photocurrent \( J_{ph} \) is normally defined as:

\[
J_{ph} = q \varepsilon \left( \mu_n \Delta n + \mu_p \Delta p \right),
\]

where \( \varepsilon \) is the electric field, \( q \) is the charge of an electron, \( \mu_n \) and \( \mu_p \) are the mobility of electrons and holes, respectively. For a p-type semiconductor (\( \rho \gg n \)), \( J_{ph} \) is mainly dependent on \( \Delta p \). Hence, \( J_{ph} \approx q \varepsilon \mu_p \Delta p \).

In accordance with the photoconductivity theory of amorphous semiconductors, \( \Delta p \) at room temperature can be written as:

\[
\Delta p_i = G \exp \left( \frac{\phi - (E_i - E_F)}{kT} \right),
\]

where \( \phi \) is the activation energy and \( E_i \) the valence band. This equation, together with (3) and (4), describes the strain-induced photoconductive process in its entirety.

Now that we have a strain-modified photoconductivity theory of Co-C films, we look into their characteristics in more detail by examining two distinct ranges: weak strain and strong strain. In the case of weak strain (\( s \to 0 \)), as shown in Fig. 2a, equation (3) reduces to:

\[
G = \frac{np}{n+p} \rho \nu X^\nu \exp \left( \frac{\gamma_\nu s}{kT} \right) \left\{ \sum_{i=1}^{N} \exp \left( \frac{-\Delta E_t}{kT} \right) + \sum_{j=1}^{M} \exp \left( \frac{-\Delta E_j}{kT} \right) \right\},
\]

where we assume \( \gamma_p = \gamma_n = \gamma_\nu \). From equations (4), (5) and (6), we have:

\[
J_{ph}(s) = J_0 \exp \left( \frac{\gamma_\nu s}{kT} \right).
\]

Equation (7) shows that \( J_{ph} \) increases exponentially with weak strain in Co-C films. Further, for amorphous semiconductors with a small value of \( \gamma_\nu \), the equation implies that \( J_{ph} \) may be linear with strain \( s \).

In the case of strong strain (see Fig. 2b), the trap levels may penetrate \( E_i \) and \( E_j \), thereby causing \( \exp \left( \frac{-\Delta E_t}{kT} \right) \) and \( \exp \left( \frac{-\Delta E_j}{kT} \right) \) to be small. Similar to the calculation process for weak strain, we have:

\[
J_{ph}(s) = J_{max} \left[ 1 - \alpha \exp \left( \frac{-\gamma_\nu s}{kT} \right) \right],
\]

where \( \alpha \) can be a constant determined by experimental results or by equations (3), (4) and (5). Equation (8) exhibits the saturation behavior of the photocurrent of Co-C films under strong strain. It is worth noting that maximum photocurrent \( J_{max} \) depends on the number of discrete states at \( E_i \) and \( E_j \), rather than \( \gamma_\nu \).

Fig. 3a shows that the out-of-plane compressive strain [defined as \( s_{out} = \frac{c(V - c(V = 0))}{c(V = 0)} \)] increases linearly with the bias voltage. In fact, out-of-plane expansion would be accompanied by contraction in both in-plane directions of PMN-PT single crystal. With the out-
of-plane strain equal to 0.2%, the in-plane tensile strain \( s_{in} \) was calculated as \(-0.1\%\) by Poisson relation \( s_{in} = -\frac{2\mu}{1-\mu} s_{out} \) using Poisson ratio \( \mu = 0.214^{+2,22} \). The in-plane tensile strain in the PMN-PT substrate can be transferred to the Co-C film. Thus, the absolute value of \( s_{in} \) is an appropriate substitute for the strain in the Co-C film. Fig. 3b illustrates the theoretical and experimental photocurrent as a function of \( s_{in} \) in Co-C films. To reduce the influence of relaxation effect in the PMN-PT substrate, we investigated photoc conductivity with the bias voltage slowly increased from 0 to 500 V. Strain-modified sensitivity \( \gamma_0 \) is calculated as \(117.3 \text{ eV from the experimental data.} \) The fit parameters used to generate the fit curve in Fig. 3b were: \( J_0 = 7.6 \times 10^{-5} \text{ mA/cm}^2, J_{max} = 0.247 \text{ mA/cm}^2, \alpha = 7.06 \). The theoretical simulation is highly consistent with the experimental data. In the strain range of \( 0 \sim 0.04\% \), the photocurrent exhibits an exponential increase with strain, whereas saturation behavior is observed in the strain range of \( 0.08 \sim 0.1\% \). Both phenomena are predicted by the proposed strain-modified photoc conductivity theory.

In comparison with pure a-C films, Co-C films exhibit a significant strain-modified photoc conductivity. The discrete states at \( E_F \) and \( E_g \) are known to originate primarily from defects. Co-doping may influence the medium-range order in Co-C films, thus favoring the generation of these discrete states\(^{20} \). The relation \( J_{max} \sim M + N \) also means that the maximum photocurrent is enhanced by Co-doping. The model is not confined to the Co-C film system. The shapes of the photocurrent-strain characteristics are dependent on the magnitude of strain sensitivity \( \gamma_0 \) as determined by amorphous materials. In some systems with a small \( \gamma_0 \), no saturation behavior may be observed. In addition, strain-modified sensitivities \( \gamma_p \) and \( \gamma_n \) are not necessarily constants. They may be tuned by temperature or even by strain itself. In this case, \( \gamma_p(T,s) \) and \( \gamma_n(T,s) \) can be used to replace \( \gamma_0 \) when describing photoc conductivity sensitivity to strain.

In summary, thin Co-C films were grown on PMN-PT substrates, and the effects of strain were investigated by applying electric fields to piezoelectric PMN-PT. Under illumination, a significant degree of photoc conductivity was observed with an increase in strain. A strain-modified photoc conductivity theory was then developed to elucidate the possible mechanism of this remarkable phenomenon. The basic model shows that the band gap can be tuned by strain, thus inducing photoc conductivity from nothing. The photocurrent simulated using the model shows strong consistency with the experimental data. In addition to Co-C films, the theory proposed herein may also be applied to other amorphous material systems.

Methods

Samples preparation. Co-doped and undoped a-C films were grown on substrates of (001) oriented PMN-PT using the pulsed laser deposition method. Before deposition, the PMN-PT substrates were ultrasonically cleaned in ethanol, and then acetone, and finally rinsed in deionized water. The deposition chamber was pumped to \( 6 \times 10^{-3} \text{ mbar, and the substrates were heated to } 400 \text{ C. A graphite disk with } >99.99\% \text{ purity embedded with a strip of cobalt (99.9%) was used as the target. Deposition was performed using a KrF excimer laser with } 320 \text{ mJ/pulse energy and a frequency of } 5 \text{ Hz for } 10 \text{ min.} \)

Microstructure observation. A scanning electron microscope (JEOL JSM-7001F, Japan) was used to observe the surface morphology and thickness (20 nm) of the samples. The Co concentration was analyzed via energy-dispersive X-ray spectroscopy, and found to reach 10%. Transmission electron microscopy (TEM) was performed using an FEI Tecnai G2 20 scanning TEM at 200 kV, and X-ray diffraction (XRD) was used to investigate the lattice displacement of the PMN-PT substrate with the application of external strain. Raman spectroscopy with a 514-nm laser (WITec-Alpha, Germany) was used to identify the disordered structures and measure the sp\(^2\)/sp\(^3\) ratio, with Raman spectra acquired in the range of \( 1000 \sim 1800 \text{ cm}^{-1} \).

Electric measurement. Silver surface electrodes were evaporated on the Co-C films to ensure an ohmic contact. The resistance, current-voltage (I-V) relations and photocconductivity of the Co-C films were measured using the standard four-probe method with a Keithley 2400 SourceMeter. Monochromatic light illumination was provided by a semiconductor laser (wavelength \( \lambda = 532 \text{ nm} \)) with variable power density, and the DC voltage across the PMN-PT was supplied by a Keithley 6487 voltage source. To limit the possibility of substrate crack as a result of polarization reversal, most measurements were carried out in a moderate range of \([-300 \text{ V, 500 V}] \).


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**Author contributions**

J.G. proposed and led the project. Y.C.J. conceived the idea, designed the experiments and developed the theory. Y.C.J. and J.G. wrote the manuscript and prepared all figures together.

**Additional information**

Competing financial interests: The authors declare no competing financial interests.

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