Optical manipulation of localized electron transport in disordered chromium nitride

Bidesh Biswas^{1,2} Deeksha Sharma^{1,2} Sourav Rudra^{1,2} Dheemahi Rao^{1,2} Akhil Tayal^{3,3}

Ashalatha Indiradevi Kamalasanan Pillai^{,4} Magnus Garbrecht^{,4} N. S. Vidhyadhiraja^{,5,6} and Bivas Saha^{,2,6,*}

¹Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India ²International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India

³Deutsches Elektronen-Synchrotron DESY, 22607 Hamburg, Germany

⁴Sydney Microscopy and Microanalysis, The University of Sydney, Camperdown, New South Wales 2006, Australia ⁵Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India ⁶School of Advanced Materials, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India

(Received 18 April 2024; revised 26 June 2024; accepted 28 January 2025; published 10 February 2025)

Localization of quasiparticles in disordered and amorphous environments is one of the most intriguing phenomena of condensed matter physics. Thus far, temperature-induced inelastic scattering and magnetic field-induced time-reversal symmetry breaking are the widely known methods to manipulate electron localization in materials. Here, we show conclusive experimental evidence of the photoinduced manipulation of localized electron transport in a prototype-disordered system, chromium nitride (CrN). We inspect this phenomenon by establishing a strong correlation between the temperature-dependent photoconductivity response and the electronic state of CrN. In metallic CrN, the photoresponse is consistently negative, while in semiconducting films, it is positive. However, CrN films exhibiting localized electronic transport at low temperatures exhibit a positive-to-negative photoresponse transition, which we explained through the light-induced breakdown of electron phase coherence responsible for the electron localization and the recharging of traps upon high-intensity photoirradiation mechanisms. Our results illustrate the optical manipulation of electron localization and hold great potential for achieving on-demand localization control for adaptive device applications.

DOI: 10.1103/PhysRevB.111.085302

I. INTRODUCTION

The quantum self-interference of noninteracting particles in a disordered environment constitutes some of the most intriguing phenomena in condensed matter physics [1-4]. One of the most striking outcomes of self-interference is the localization of carriers (electrons, phonons, exciton, polariton, etc.) that leads to an absence of diffusion in disordered or amorphous semiconductors and bad metallic systems [5-8]. The strength of the localization strongly depends on the disorder or randomness density. Materials with low structural and topological disorder exhibit weak electron localization, whereas when the disorders become sufficiently large, it induces strong electron localization, known as the Anderson localization. Ever since the initial discovery by Anderson [1], electronic localization has attracted significant interest in the quest to understand not only the fundamental physics of carrier transport in disordered materials, but also their applications in many device technologies [9–14].

Traditionally, electron localization in materials has been tuned with temperature-induced inelastic scattering and externally applied magnetic fields [15–18]. In the localized transport regime, an increase in the system temperature leads to enhanced electron-phonon scattering, which induces

decoherence and destroys the localization [19,20]. As a result, electron localization fades away at higher temperatures. In addition, magnetic field or magnetic impurities [16,21] also dismantle the localization phenomenon by breaking the time-reversal symmetry that quenches the coherent backscattering of the electrons. Though the two methods mentioned above are used extensively to study electron localization, the development of other readily available external variables that can tune and control electron localization would greatly help both in fundamental physical studies and on-demand localization control for reconfigurable device applications. Numerous device technologies like electrophotographic copiers, liquid crystal displays, bistable memory, memristors, optical disks, photonics, and thin-film transistors rely on disordered/amorphous semiconductors where the device performance is influenced by the level of disorder. For instance, the quantum efficiency and longevity of InGaN/GaN light-emitting diode devices are significantly affected by the degrees of disorder in the system [22]. Implementing localization control provides tunable electrical conductivity, allowing on-demand modulation of performance in these devices.

Optical illumination is one of the most well-established and widely used external variables to tune the physical properties of materials. Photosensitive materials are heavily used in practical device implementations such as photodiodes, phototransistors, photoinduced metal-insulator phase transition [23–29], photochromic smart windows, etc. Though high-

^{*}Contact author: bsaha@jncasr.ac.in; bivas.mat@gmail.com

intensity photon pulses in the form of lasers have been used extensively to understand the dynamics and relaxation of electrons in many classes of materials [30,31], not much attention has been devoted to understanding and tuning electron localization with light. However, recent research has shown that in the presence of strong exciton-phonon coupling in organic semiconductors, the excitons can access the higher-lying delocalized states for a short time, which allows them to transport over a large distance [32-34]. Such phonon-mediated transient delocalization phenomenon holds great promise in fundamental understanding and improving the carrier transport in disordered materials. However, similar studies with excitons, electrons, or photons in any inorganic material systems are relatively uncommon [35-38]. In this work, we show photoinduced electron localization control in a disordered metallic system, chromium nitride (CrN).

Unstrained CrN epitaxial films exhibit a simultaneous magnetic, structural, and electronic first-order phase transition at a Néel temperature $(T_N) \sim 277$ K (aligning with the T_N ranges between 260-285 K [39-43] reported for bulk and relaxed thin films in the literature). At high temperatures $(T > T_N)$, CrN shows a rocksalt crystal structure with a semiconducting and paramagnetic state. However, as the temperature is lowered below T_N , antiferromagnetic spin alignment leads to a large magnetic stress that drives a structural transition from the rocksalt-to-orthorhombic phase [44-46]. Concomitant to the magnetic and structural transition, the electronic state of CrN also changes from a charge-order insulator to a disordered metallic system below the T_N [40,47]. Unlike in many strongly correlated oxides such as VO₂, NdNiO₃, etc., where strong electron correlation and/or Peierls instability causes the phase transition and leads to a low-temperature insulating phase [48,49], the metalinsulator transition in CrN is caused by anisotropic magnetic stress. The magnetic stress-driven phase transition in CrN is unique and has been demonstrated experimentally by carefully engineering the epitaxial strain [50].

In CrN, as chromium and nitrogen vacancies are thermodynamically stable [51,52], it is inherently a disordered material. Therefore, the ultrasensitivity of the CrN's electronic structure on its stoichiometry can be leveraged in preparing thin films that exhibit markedly different low-temperature electronic transport behavior ranging from metallic, localized, and strongly localized regimes. Figure S1 [53] illustrates the diverse temperature-dependent electron transport behavior of six different CrN thin films we obtained through variations in Cr:N₂ flux ratio, substrate temperature, deposition pressure, and strain in the film (See Supplemental Material (SM) [53] for details). As a result, CrN is an ideal inorganic material for exploring the photoinduced manipulation of electron localization phenomena. In this work, we utilize this unique feature of the electronic structure of CrN to show photoinduced localization control with light.

temperature of 800 °C and a deposition pressure of 10 mTorr, showcasing a prominent characteristic metal-insulator transition (MIT). In this instance, the Cr target power was set to 25 W. For the second film [depicted in Fig. 1(c)], identical deposition conditions were employed; but with a Cr target power of 50 W. In contrast, the third film [depicted in Fig. 1(d)] was deposited at room temperature under a deposition pressure of 10 mTorr, with the Cr target power set to 25 W. The Ar: N_2 ratio was fixed at 9:6 in all three films. The thicknesses of the films are 240 nm. Details on the sample's electronic resistivity, photoconductivity, and other measurement techniques are presented in SM [53].

III. RESULTS AND DISCUSSION

A. Diverse low-temperature resistivity

Optimized growth conditions utilized in the first film results in epitaxial, and single-crystalline CrN films exhibiting electronic localization $(\frac{\partial \rho}{\partial T} < 0)$, where ρ is electrical resistivity) at low temperatures (T < 150 K) [see Figs. 1(a) and 1(b)]. Such localization stems from the coherent backscattering of electrons from different point defects like oxygen impurities (O_N) , chromium and nitrogen vacancies (V_{Cr}, V_N) , interstitials (Ni), etc. However, the localization behavior fritters away at higher temperatures, and the disordered metallic phase $(\frac{\partial \rho}{\partial T} >$ 0) appears with an increase in resistivity until the MIT point at ~277 K. After the phase transition at T_N , CrN exhibits semiconducting electronic behaviour with decreased resistivity $\left(\frac{\partial \rho}{\partial T} < 0\right)$ at higher temperatures. Hall measurements show an *n*-type carrier concentration of $2.2 \times 10^{19} \,\mathrm{cm}^{-3}$ at room temperature due to electronically active defects. Arrheniustype thermal activation corresponding to the bandgap and trap-states-enabled transitions is also observed at high temperatures (See Fig. S2-3 in SM for details [53]).

Compared to the nearly stoichiometric film, CrN deposited with lower nitrogen flux [Fig. 1(c)] exhibits a fully metallic phase at low temperature. However, semiconducting transport is observed beyond the MIT point at \sim 277 K. Here, the abundance of nitrogen vacancies results in high electron concentration of 1×10^{21} cm⁻³ and resistivity of ~26 times smaller than the film showing electronic localization. In contrast with the first two cases, when the growth temperature is lowered and a third film is deposited, the electronic phase changes drastically to the strongly localization regime [Fig. 1(d)]. Lower growth temperature presumably introduces a large density of defects and disorders that leads to the insulating film with low-temperature resistivity ~ 2000 times higher than the first film. Fitting the resistivity-vs-temperature with the Mott variable range-hopping (MVRH) mechanism leads to a high characteristic Mott temperature $T_M = 1 \times$ 10⁶ K (see Fig. S4 in SM [53]), highlighting the highly localized electron transport in the film.

II. THIN-FILM SAMPLE PREPARATION

Three distinct CrN thin films, each demonstrating varied resistivity behaviors, are deposited via ultrahigh-vacuum magnetron sputtering at a base pressure of 1×10^{-9} Torr. The first CrN film [depicted in Fig. 1(b)] is deposited at a high substrate

B. Temperature-dependent photoconductivity

Photoconductivity measurements with a Xe-arc lamp (400-2400 nm) show that the first CrN film showing localized electron transport exhibits a positive photoresponse above the MIT at 300 and 350 K. Since CrN exhibits semiconducting properties at high temperatures, such positive photoconduc-



FIG. 1. (a) Schematic showing the optical manipulation of electron localization. Upon photoexcitation, enhanced electron scattering from photogenerated phonons, electron-phonon, and anharmonic phonon interactions leads to the breakdown of the electron phase coherence responsible for localization. (b)–(d) Temperature-dependent resistivity of CrN thin films in the 50–400 K temperature range. The diverse low-temperature resistivity behavior is achieved through precise control over Ar:N₂ gas ratio and substrate temperature during the growth. (b) The resistivity of CrN film shows localization in the low-temperature region. With increasing temperature, localized CrN transitions into a metallic region, followed by the metal-insulator phase transition at ~277 K. (c) The temperature-dependent resistivity of CrN film shows metallic conductivity at low temperatures and metal-insulator transition at T_N . (d) The temperature-dependent resistivity of CrN exhibits strong electronic localization and no apparent electronic phase transitions. (e) Temperature-dependent photoconductivity measurements [for the film in Fig. 1(b)] show that semiconducting ($T > T_N$) and metallic (from 150 K to T_N) CrN exhibit a positive and negative photoresponse, respectively. However, as the localization sets in at lower temperatures (T < 150 K), photoconductivity undergoes a negative-to-positive transition. A fixed light intensity of 32 mW/cm² is used for these measurements. (f) In the localized regime (T = 80 K), CrN exhibits a positive photoconductivity for low light intensity. However, as the light intensity increases, the photoconductivity undergoes a positive-to-negative transition, indicating modification of localized electronic transport upon high-intensity photoirradiation.

tivity is normal and represents the photoinduced carrier generation that enhances the conductivity. The persistence in the photogeneration and decay arises due to the trapping of photogenerated electrons at the defect states [51,54] (see Fig. S5 in SM [53]). Interestingly, as the temperature is reduced below T_N , photoconductivity undergoes a positive-to-negative transition. Such a positive-to-negative photoconductivity transition is interesting but expected, as CrN undergoes a semiconducting-to-disordered metallic electronic transition. Here also, the persistence in photoconductivity is observed due to the trapping of photogenerated carriers. The negative photoresponse has been found previously in degenerate nitride semiconductors such as InN, ScN [55,56], and other metallic materials such as Au, Te nanowires [57,58], etc.

The negative photoresponse is observed until 150 K. Interestingly, at 100 and 80 K, the photoconductivity turns positive again. The magnitude of the positive photoconductivity increases with the decrease in temperature [Fig. 1(e)]. Electronically, the region below 150 K corresponds to the localized regime, where conduction is mediated by the MVRH mechanism. Therefore, the temperature-dependent photoresponse correlates with the electronic states of CrN, positive with high photoconductivity in the semiconducting region $(T > T_N)$, negative in the metallic region (150–277 K), and positive again with lower overall but increasing with a decrease in temperature in the localized regime (T < 150 K).

Further, light-intensity dependent photoresponse at 80 K shows that photocurrent is positive at lower intensities of the incident light [32 and 47 mW/cm^2 in Fig. 1(f)]. However, as the intensity increases (73 and 110 mW/cm^2), photocurrent exhibit mixed behavior, positive initially upon the impingement of light, which gradually turns into negative. The photoresponse exhibits a purely negative characteristic with a further increase in the incident light intensity



FIG. 2. (a) Temperature-dependent photoconductivity of the second CrN film exhibiting fully metallic phase at low temperature shows positive photoresponse above $T_N \sim 277$ K and negative photoconductivity below T_N . (b) Temperature-dependent photoconductivity reveals positive photoresponse at all temperatures for the third film having strong electron localization without the metal-insulator transition. The persistence in the photogeneration and decay appears due to the presence of traps. (c) Temperature-dependent EXAFS analysis of the first CrN film that exhibits metal-insulator transition depicted in (a). The peak corresponding to Cr–Cr bond splits into two (marked with an arrow) upon structural transition at low temperature. (d) Temperature-dependent EXAFS analysis of the third CrN film [Fig. 2(d)] without metal-insulator transition. The Cr–Cr peak does not split at low temperatures, indicating the absence of structural transition. (e) The STEM imaging. (f) HRTEM shows excellent structural quality of the films. The electron diffraction pattern at the inset shows cube-on-cube epitaxy. (g) Elemental mapping of Cr and N atoms showing the uniform distribution of Cr and N inside the film.

 $(\geq 123 \text{ mW/cm}^2)$. The quantitative decrease in the photoconductivity also increases with an increase in the light intensity. Such negative photoresponse is similar to the behavior observed in the film's delocalized metallic region (150 K < T < T_N). Therefore, this transition of photoresponse from positive to negative with the increase in light intensity indicates the possibility of a change in the electronic transport in CrN from a localized hopping to delocalized metallic-like transport upon light irradiation. In addition, recharging of defect centers upon photoirradiation in CrN could also impact the mobility of charge carriers through enhancement of ionized impurity scattering and the formation of long-range Coulomb potential, giving rise to opposite signs of photoconductivity. Discerning the above two mechanisms is not readily possible and may require ultrafast measurements and deconvolution of different processes.

To further establish the correlation between photoconductivity and temperature-dependent electronic state in CrN, temperature-dependent photoconductivity of the other two CrN films exhibiting metallic and highly localized electron transport are studied [refer to Figs. 1(c) and 1(d)]. At room temperature, a positive and persistent photoconductivity is observed in both films, similar to the photoresponse observed in the first film [at 300 K in Figs. 2(a) and 2(b)]. However, for CrN exhibiting a metallic phase, the positive photoresponse turns to negative below the T_N , and remains negative below 150 K, which is consistent with its metallic nature [Fig. 2(a)]. In contrast, the photoresponse of the second film [refer to Fig. 1(d)], having a higher degree of electron localization, remains positive in the entire temperature range [Fig. 2(b)]. Importantly, the sign of the photoconductivity does not change upon changes in the light intensity in both the cases (details in

Appendix B). Thus, the photoconductivity measurements reveal a striking correlation between the electronic states and the sign of the photoresponse across the metal-insulator transition regime of CrN. The positive photoconductivity is exclusively associated with the semiconducting and localized electronic states, and the negative photoresponse is exclusively associated with the metallic state. Thus, light-intensity dependent positive-to-negative transition of photoconductivity in localized electron transport.

C. Structural transition

The concomitant structural transition and crystal quality of the films are probed with temperature-dependent extended x-ray absorption fine structure (EXAFS) and high-resolution transmission electron microscopy (HRTEM). The rocksaltto-orthorhombic structural transition in CrN is such that the Cr-Cr bond distance shrinks and expands along two mutually perpendicular directions due to anisotropic magnetic stress [45] (see Fig. S6 in SM [53]). Figures 2(c) and 2(d) shows the EXAFS analysis across the Cr K edge in a radial distance of the coordination sphere up to ~ 4 Å. For the CrN films with metal-insulator electronic phase transition [Figs. 1(b) and 1(c)], the peak corresponding to the Cr–Cr bond splits into two (marked with arrow) below the transition temperature $T_N \sim$ 277 K [Fig. 2(c)]. However, the film with no metal-insulator transition [Fig. 1(d)], the Cr-Cr peak does not split into two upon cooling the film below T_N . The crystal quality of the film exhibiting localization is shown in Figs. 2(e) and 2(f). The films grow along with (002) orientations on MgO (001) substrate with cube-on-cube epitaxy (see Figs. S7 and S8 in



FIG. 3. (a) Temperature-dependent resistivity of CrN films with increasing disorder strength from S1 to S4. All four films exhibit a metalinsulator transition at ~277 K. (b) The photoresponse of the films at a fixed light intensity of 240 W/cm² at 80 K (200 K for S4). (c) $\ln \sigma$ -vs- $T^{-0.25}$ plot for the films to quantify the disorder strength. Film S1 contains the least disorder density and S4 is has the highest disorder density.

SM [53]). The Cr and N atoms are uniformly distributed inside the films [Fig. 2(g)].

The structural characterization confirms the origin of the temperature-independent positive photoconductivity observed in the second film [Fig. 2(b)]. As the rocksalt-to-orthorhombic structural transition is absent in this film, the corresponding insulator-to-metal transition also did not occur, and hence the photoconductivity remains positive in the whole temperature range. However, when there is a rocksalt-to-orthorhombic structural transition, the corresponding electronic phase also undergoes insulator-to-metal transition; hence, the photoconductivity also changes from positive to negative.

D. Disorder-dependent photoconductivity

Additionally, to assess the impact of the strength of the disorder on the light-induced localization-to-delocalization electronic transition, four different CrN films (see SM [53] for details about the growth conditions) exhibiting varying degrees of the disorder are prepared. All the films exhibit the characteristic metal-insulator transition at \sim 277 K [Fig. 3(a)]. However, the temperature corresponding to the onset of the localization in them progressively increases with the increase in the disorder strength. To quantify the strength of localization, their temperature-dependent electrical resistivity in the low-temperature regime is fitted with the MVRH ($\sigma =$ $\sigma_0 e^{-(T_M/T)^{0.25}}$) model. T_M in the MVRH is the characteristic Mott temperature, which signifies the degree of disorder and can be obtained from the slope of the $\ln \sigma$ -vs- $T^{-0.25}$. Also, in MVRH, the activation energy is not constant and varies with temperature with the relation $E_a = 0.25kT^{0.75}T_M^{0.25}$. Since changes in the growth conditions lead to different concentrations of vacancies and disorders, the strength of localization changes, as shown in Table I. The T_M is small for the first two films (S1 and S2); therefore, the activation energy is low.

However, for the S3 and S4 CrN, the strength of localization and, therefore, T_M and the activation energy, increase drastically.

Photoresponse measurements (at 80 K for S1, S2, and S3, and 200 K for S4 with an incident light intensity of $\sim 240 \text{ mW/cm}^2$) reveal negative photoconductivity for the S1 and S2 and positive photoconductivity for the S3 and S4 films [Fig. 3(b), Appendix C]. As the incident light intensity is sufficient to cause the electronic delocalization in the first two films, a negative photoresponse is observed. However, in the last two films, the intensity of the incident light is insufficient to cause delocalization, resulting in a positive photoresponse. These results, therefore, strongly demonstrate the photoinduced and tunable localization control with varying degrees of disorder density.

E. Origin of photoinduced delocalized transport

To explain the origin of the tunable photoconductivity, we consider two different mechanisms: the role of photoinduced generation of phonons, which affects the transport properties of CrN, and the role of recharging of defects upon photoirradiation. For the first mechanism, the electronic densities of states (DOS) of CrN in the localized and itinerant metallic

TABLE I. Fitted disorder temperature and activation energy obtained from the ln σ vs $T^{-0.25}$ plot.

| Sample | T_M (K) | $E_a ({\rm meV})$ |
|-----------|----------------------|-------------------|
| <u>S1</u> | 2.7 | 0.75 |
| S2 | 11.4 | 1.05 |
| S3 | 1.47×10^{3} | 3.5 |
| S4 | $1.5 	imes 10^6$ | 20.48 |



FIG. 4. (a) Qualitative DOS of CrN at T < 150 K. The presence of disorder localizes (red gridded region) the electronic states near the band tail. The mobility edge (E_M) separates the extended and localized electronic states. The Fermi level is inside the localized region that facilities the MVRH conduction. (b) DOS of CrN upon shining of low-intensity light. The relaxation of photogenerated electrons through the generation of phonons and electron-phonon coupling transiently delocalizes the electronic states. The electron conduction is still dominated by the MVRH type. (c) DOS of CrN upon shining of high-intensity light. A large density of photogenerated phonons could lead to inelastic scattering that results in decoherence and breakdown of electron localization. The Fermi level shifts above the mobility edge, facilitating metal-like conductivity.

regime are analyzed (details in Appendix D). Moreover, the changes in the DOS due to the light irradiation are further investigated qualitatively. Figure 4(a) presents the DOS of antiferromagnetic CrN with depleted electronic states near the Fermi level [44,45,59]. Here, the presence of disorder localizes (red gridded region) the electronic states near the band tail. The localized states are random in both Euclidean and energy space and follow a Gaussian distribution pattern. The mobility edge (E_M) separates the extended and localized electronic states. As the Fermi level is deep inside the localized region, the electron conduction is mediated by the MVRH. Upon low-intensity light irradiation at 80 K, the photogenerated electrons relax through the generation of phonons [Fig. 4(b)]. Phonon generation through other channels like electron-phonon coupling, anharmonic phonon scattering, and photon-phonon coupling are also possible mechanisms that enhance phonon population upon photoirradiation. The Fermi level still remains below the mobility edge, and the conduction is MVRH type. Thus, the phonons generated through the relaxation of photoelectrons assist in the hopping of electrons across the energy threshold, which results in positive photoconductivity.

However, it is important to note that phonon-assisted hopping is inelastic, gradually introducing noncoherence in the system [19,20]. When the phonon density is high due to the relaxation of the photogenerated electrons in large numbers at a higher light intensity, the coherent backscattering, responsible for the localization, starts to fade away. As a result, the electronic states become delocalized transiently [Fig. 4(c)]. The electrons near the Fermi level become itinerant and can transport over a large distance, thus facilitating a metal-like negative photoconductivity in CrN.

The same model also explains the origin of negative photoconductivity observed in the metallic phase of CrN (150 K $< T < T_N$). In general, the negative photoconductivity in metal stems from the enhanced charge-carrier scattering through several mechanisms like intraband electron-electron

scattering, plasmonic hot electronic scattering, electronphonon scattering, etc. [58]. However, given the electron density of CrN $\sim 1 \times 10^{19}$ cm⁻³, much smaller than regular metals like Au and Ag ($\sim 6 \times 10^{22}$ cm⁻³), the first two mechanisms are most unlikely to cause negative photoresponse. Hence, the scattering of electrons from enhanced electronphonon scattering and charged defects is a plausible origin of negative photoconductivity in metallic CrN.

While our primary focus has been on the phonon effects to explain the positive-to-negative photoconductivity transition, it is essential to acknowledge the significant role of charge defects in influencing electronic transport under light illumination. CrN exhibits a natural propensity to form both chromium vacancies (V_{Cr}) and nitrogen vacancies (V_N) simultaneously [51,54]. Additionally, the high oxygen affinity of Cr leads to the formation of substitutional oxygen defects (O_N) in CrN, which act as *n*-type defects [54]. A prolonged exposure of CrN films in ambient conditions could also lead to surface oxidation. The presence of point defects such as V_{Cr} , V_N , and O_N creates a disordered system in CrN, significantly impacting its transport properties.

At 80 K, when the thermal energy of electrons is low, the delocalized electrons in CrN get trapped at $V_{\rm N}/O_{\rm N}$ or other defect centers, and resistivity increases with the decrease in temperature. Upon irradiation with high-intensity photons, the trapped electrons are released, becoming delocalized, forming charged-defect centers [Fig. 5(a)]. This significantly enhances ionized-impurity scattering and reduces carrier mobility, which could cause the photocurrent to become negative. The presence of ionized-impurity scattering was found to have a substantial impact on the carrier mobility in a sister transition-metal nitride compound ScN recently [60]. Besides, the formation of built-in potential by charged defect could also impede the transport of electrons, leading to decreased photoconductivity. Therefore, under low-intensity light irradiation, when the density of charged defects remains low, it results in positive



FIG. 5. (a) Schematic of neutral-to-charged defect formation upon photoirradiation. The delocalization of electrons with highintensity light creates charged defects in CrN. (b) Temperaturedependent mobility of CrN with resistivity is demonstrated in Fig. 1(b). In the delocalized metallic region ($T < T_N$), the mobility decreases with the rise in temperature.

photoconductivity. However, as the light intensity increases, the density of charge defects rises significantly, reducing carrier mobility and making the photoconductivity increasingly negative.

In the metallic region $(150 \text{ K} < T < T_N)$, the density of charged defects is significant due to the thermal activation of defects. This leads to enhanced electron charged-defect scattering, which reduces carrier mobility [Fig. 5(b)], evident from the temperature-dependent mobility data of CrN, showing a nearly 30% decrease in mobility as the temperature increases from ~100 K to approximately 270 K. Upon light exposure, the density of charged defects increases further, intensifying carrier-defect scattering and resulting in negative photoconductivity. In the semiconducting region $(T > T_N)$, the increase in photoexcited carrier density suppresses the effects of scattering, leading to positive photoconductivity in this regime. Therefore, the influence of the charged defects and their impact on electronic transport may also explain the observed tunable photoconductivity in CrN along with the influence of photoinduced phonon. As mentioned earlier, a more comprehensive study is necessary to elucidate further the precise origin of the diverse photoconductive responses in CrN.

IV. CONCLUSION

In summary, we show the photointensity-controlled modulation of localized electron transport in a disordered metallic system, CrN. From a fundamental perspective, our work presents an insight into the optical manipulation of electronic localization and the correlated electronic transport. This contrasts the temperature and magnetic-field induced tunability of localization used traditionally for localization control. Furthermore, demonstrating tunable photoconductivity across the metal-insulator phase would enable CrN as a material for reconfigurable device applications. We believe the observed phenomenon can also be extended to modulate and improve the transport properties in other technologically important disordered materials and improve their device efficiency.

ACKNOWLEDGMENTS

B.B. and B.S. acknowledge International Centre for Materials Science (ICMS) and Sheikh Saqr Laboratory (SSL) in JNCASR for support. B.S. acknowledges the Young Scientist Research Award (YSRA) from the Board of Research in Nuclear Sciences (BRNS), Department of Atomic Energy (DAE), India by Grant No. 59/20/10/2020-BRNS/59020 and Anusandhan National Research Foundation (ANRF) in India for a Core Research Grant No. CRG/2023/007061 for financial support. Parts of this research were carried out at PETRA III beamline P64. Beamtime was allocated for Proposal No. I-20220131. Financial support by the DST provided within the framework of the India@DESY Collaboration is gratefully acknowledged. The authors greatly acknowledge Prof. T. V. Ramakrishnan (Indian Institute of Science, Bangalore) for helpful comments and discussions.

B.B. and B.S. conceived this project; B.B. deposited the thin films and performed the electrical measurements; D.S. performed the photoconductivity measurements with assistance from D.R. and B.B.; S.R. and B.S. performed the theoretical modeling; A.T. and B.B. performed the synchrotron EXAFS measurement and analysis; A.I.K.P. performed the Transmission Electron Microscopy (TEM) sample preparation and M.G. performed the TEM imaging; and N.S.V. contributed to the theoretical interpretation with B.B. and BS. All authors discussed and contributed to the preparation of the manuscript.

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.



FIG. 6. (a) Intensity-dependent photoconductivity of metallic CrN at 200 K. The photoconductivity remains negative despite the increase in intensity of the incident light. (b) Intensity-dependent photoconductivity of the localized CrN film [film with temperature-dependent resistivity shown in Fig. 1(b)] measured at 300 K. The photocurrent increases with the increase in light intensity, and no reversal of photocurrent is observed as in the case of localized region. The percentage values in the figure indicate the fraction of the total source power.



FIG. 7. Wavelength-dependent photoconductivity of localized film (a) [Fig. 1(b) in main manuscript] and heavily localized (b) [Fig. 1(d) in main manuscript] CrN films measured at room temperature. The photoresponse is positive in both cases with a small variation in photocurrent upon irradiation of light of different wavelengths.

APPENDIX A: ORIGIN OF DIVERSE LOW-TEMPERATURE RESISTIVITY BEHAVIOR IN CrN

The diverse low-temperature resistivity behavior observed in chromium nitride (CrN) stems from a synergistic interplay of multiple factors, such as the $Cr:N_2$ flux ratio, substrate temperature, and deposition pressure. Theoretical work and previous experimental findings [51,54] have shown that whereas the Cr vacancy in CrN functions as a donor-type defect, the N vacancy in CrN serves as an *n*-type dopant. Consequently, the films deposited at higher Cr flux led to metallic (degenerate) semiconducting behavior. In the most adverse scenario, the large concentration of Cr results in phase segregation, leading to the formation of metallic Cr₂N phase leading to metallic conductivity in the full temperature range. Higher N₂ flux during film deposition correlates with a progressive rise in resistivity, ultimately resulting in a transition to *p*-type conductivity. In terms of growth temperature, opting for a higher growth temperature yields an epitaxial film with enhanced conductivity. In contrast, films deposited at lower growth temperatures tend to be polycrystalline (textured), resulting in resistive behavior.

APPENDIX B: INTENSITY AND WAVELENGTH-DEPENDENT PHOTORESPONSE OF CrN

1. Intensity-dependent photoresponse

The intensity-dependent photoconductivity of the metallic and localized films is examined to determine whether the sign of photoconductivity changes under high-intensity photoirradiation [Fig. 6]. However, unlike the localized film at 80 K, no sign reversal of photoconductivity was observed.



FIG. 8. Temperature-dependent photoresponse of the film S3 measured at photointensity of 32 mW/cm^2 . The photoresponse is positive in the semiconducting region ($T > T_N$), and negative in the metallic region. The photoresponse turns positive again in the localized region.

2. Wavelength-dependent photoresponse

The wavelength-dependent photoconductivity of both localized and heavily localized films is analyzed [Fig. 7]. In both cases, the photo-response is positive and remains independent of the incident light wavelength.

APPENDIX C: TEMPERATURE-DEPENDENT PHOTORESPONSE OF FILM S3

To verify that the photoconductive response of the films labeled as S1–S4 are also correlated with the electronic state of CrN, the temperature-dependent photoresponse of the film S3 is measured [see Fig. 8]. Here, the photoresponse is positive in the semiconducting region $(T > T_N)$, followed by a transition into negative response in the metallic regions and again a positive photoresponse in the localized transport region, resembling the photoresponse observed in the earlier films.

APPENDIX D: COMPUTATIONAL METHODS

For rocksalt CrN, the first-principles density-functional theory implemented in VASP was used to calculate the electronic band structure and electronic density of states of CrN. For the $AFM_{[1-10]^2}$ configuration, spin-polarized calculations



FIG. 9. (a) Electronic band structure of low-temperature orthorhombic CrN calculated using U = 1. The electronic density of states (right-hand side) revealed a depleted density of states near the Fermi energy (E_f), thus a bad metallic behavior at lower temperatures. (b) The electronic density of states of rocksalt CrN with and without the presence of N vacancy (V_N). The N vacancy state acts as a donor-type defect in CrN.

with the spin moment along the *z* axis were carried out using the Generalized Gradient Approximation (GGA)+U approach with plane-wave basison partially fill 3*d* orbital of Cr [Fig. 9]. A Hubbard *U* of 1.0 eV is used in these calculations, as at higher *U* values, an electronic band gap opens up in the low-temperature phase, despite the system being a metal. The projected augmented-wave pseudopotentials are used for both the Cr and N atoms with kinetic energy cutoff of 550 eV. Gamma-centered Brillouin-zone sampling was done using 22 \times 16 *k* mesh.

- P. W. Anderson, Absence of diffusion in certain random lattices, Phys. Rev. 109, 1492 (1958).
- [2] A. Lagendijk, B. Van Tiggelen, and D. S. Wiersma, Fifty years of Anderson localization, Phys. Today 62(8), 24 (2009).
- [3] M. Filoche and S. Mayboroda, Universal mechanism for Anderson and weak localization, Proc. Natl. Acad. Sci. USA 109, 14761 (2012).
- [4] A. Dikopoltsev, S. Weidemann, M. Kremer, A. Steinfurth, H. H. Sheinfux, A. Szameit, and M. Segev, Observation of Anderson localization beyond the spectrum of the disorder, Sci. Adv. 8, eabn7769 (2023).
- [5] P. A. Lee and T. V. Ramakrishnan, Disordered electronic systems, Rev. Mod. Phys. 57, 287 (1985).
- [6] T. Yang, Y. Jin, N. B. Dahotre, Z. Wang, and A. Neogi, Temperature tunable Anderson localization and metal–insulator transition of acoustic waves in high-entropy phononic crystal, Adv. Eng. Mater. 25, 2201758 (2023).
- [7] D. Laurent, O. Legrand, P. Sebbah, C. Vanneste, and F. Mortessagne, Localized modes in a finite-size open disordered microwave cavity, Phys. Rev. Lett. 99, 253902 (2007).
- [8] B. G. Shin, J.-H. Park, J.-Y. Juo, J. Kong, and S. J. Jung, Structural-disorder-driven critical quantum fluctuation and localization in two-dimensional semiconductors, Nat. Commun. 14, 2283 (2023).
- [9] D. S. Weiss, Organic photoconductors: Photogeneration, transport, and applications in printing, in *Photoconductivity and Photoconductive Materials* (Wiley & Sons, Incorporated, John, New Jersey, USA, 2022), pp. 275–338.

- [10] D. S. Wiersma, Disordered photonics, Nat. Photon. 7, 188 (2013).
- [11] B. Lu, Y. Lu, H. Zhu, J. Zhang, S. Yue, S. Li, F. Zhuge, Z. Ye, and J. Lu, Memristors based on amorphous ZnSnO films, Mater. Lett. 249, 169 (2019).
- [12] J. F. Wager, B. Yeh, R. L. Hoffman, and D. A. Keszler, An amorphous oxide semiconductor thin-film transistor route to oxide electronics, Curr. Opin. Solid State Mater. Sci. 18, 53 (2014).
- [13] Z. Hafdi, Hydrogenated amorphous silicon thin-film transistors, in Amorphous Silicon Thin-Film Transistors: Operation, Modelling and Applications, edited by Z. Hafdi (Springer International Publishing, Cham, 2023), pp. 11–21.
- [14] Z. Jia, M. Seclì, A. Avdoshkin, W. Redjem, E. Dresselhaus, J. Moore, and B. Kanté, Disordered topological graphs enhancing nonlinear phenomena, Sci. Adv. 9, eadf9330 (2023).
- [15] G. Bergmann, Weak localization in thin films, Phys. Scr. 1986, 99 (1986).
- [16] G. Bergmann, Consistent temperature and field dependence in weak localization, Phys. Rev. B 28, 515 (1983).
- [17] K. Müller, J. Richard, V. V. Volchkov, V. Denechaud, P. Bouyer, A. Aspect, and V. Josse, Suppression and revival of weak localization through control of time-reversal symmetry, Phys. Rev. Lett. 114, 205301 (2015).
- [18] Q. D. Gibson, T. Zhao, L. M. Daniels, H. C. Walker, R. Daou, S. Hebert, M. Xanella, M. S. Dyer, J. B. Claridge, B. Slater, M. W. Gaultois, F. Cora, J. Alaria, and M. J. Rosseinsky, Low ther-

mal conductivity in a modular inorganic material with bonding anisotropy and mismatch, Science **373**, 1017 (2021).

- [19] L. Li, S. T. Lin, C. Dong, and J. J. Lin, Electron-phonon dephasing time due to the quasistatic scattering potential in metallic glass CuZrAl, Phys. Rev. B 74, 172201 (2006).
- [20] E. Abrahams, 50 Years of Anderson Localization (World Scientific, Singapore, 2010), Vol. 24.
- [21] N. Zaki, G. Gu, A. Tsvelik, C. Wu, and P. D. Johnson, Time-reversal symmetry breaking in the Fe-chalcogenide superconductors, Proc. Natl. Acad. Sci. USA 118, e2007241118 (2021).
- [22] A. E. Chernyakov, M. E. Levinshtein, P. V. Petrov, N. M. Shmidt, E. I. Shabunina, and A. L. Zakheim, Failure mechanisms in blue InGaN/GaN LEDs for high power operation, Microelectron. Reliab. 52, 2180 (2012).
- [23] H. Yoo, I. S. Lee, S. Jung, S. M. Rho, B. H. Kang, and H. J. Kim, A review of phototransistors using metal oxide semiconductors: Research progress and future directions, Adv. Mater. 33, 2006091 (2021).
- [24] J. Liu, M. Gao, J. Kim, Z. Zhou, D. S. Chung, H. Yin, and L. Ye, Challenges and recent advances in photodiodes-based organic photodetectors, Mater. Today 51, 475 (2021).
- [25] Y.-C. Lin, W.-C. Yang, Y.-C. Chiang, and W.-C. Chen, Recent advances in organic phototransistors: Nonvolatile memory, artificial synapses, and photodetectors, Small Sci. 2, 2100109 (2022).
- [26] Q. M. Liu *et al.*, Photoinduced multistage phase transitions in Ta₂NiSe₅, Nat. Commun. **12**, 2050 (2021).
- [27] K. T. Hong, C. W. Moon, J. M. Suh, T. H. Lee, S.-I. Kim, S. Lee, and H. W. Jang, Daylight-induced metal-insulator transition in Ag-decorated vanadium dioxide nanorod arrays, ACS Appl. Mater. Interfaces 11, 11568 (2019).
- [28] Y. Ru, Z. Shi, J. Zhang, J. Wang, B. Chen, R. Huang, G. Liu, and T. Yu, Recent progress of photochromic materials towards photocontrollable devices, Mater. Chem. Front. 5, 7737 (2021).
- [29] S. M. Koepfli *et al.*, Metamaterial graphene photodetector with bandwidth exceeding 500 gigahertz, Science **380**, 1169 (2023).
- [30] J. Xu, D. Chen, and S. Meng, Decoupled ultrafast electronic and structural phase transitions in photoexcited monoclinic VO₂, Sci. Adv. 8, eadd2392 (2023).
- [31] B. Liu, H. Xiao, and M. Weinelt, Microscopic insights to spin transport–driven ultrafast magnetization dynamics in a Gd/Fe bilayer, Sci. Adv. 9, eade0286 (2023).
- [32] A. J. Sneyd, D. Beljonne, and A. Rao, A new frontier in exciton transport: Transient delocalization, J. Phys. Chem. Lett. 13, 6820 (2022).
- [33] A. J. Sneyd *et al.*, Efficient energy transport in an organic semiconductor mediated by transient exciton delocalization, Sci. Adv. 7, eabh4232 (2023).
- [34] S. Giannini, A. Carof, M. Ellis, H. Yang, O. G. Ziogos, S. Ghosh, and J. Blumberger, Quantum localization and delocalization of charge carriers in organic semiconducting crystals, Nat. Commun. 10, 3843 (2019).
- [35] K.-J. Friedland, M. Hoerike, R. Hey, I. Shlimak, and L. Resnick, Giant persistent photoconductivity induced crossover from strong to weak localization in Si-δ-doped GaAs compensated with Be acceptors, Physica A 302, 375 (2001).
- [36] G. Y. Lee, B. S. Mun, and H. Ju, Observation of giant persistent photoconductivity on vanadium dioxide thin film device, Appl. Mater Today 22, 100894 (2021).

- PHYSICAL REVIEW B 111, 085302 (2025)
- [37] D. N. Bose and S. Pal, Photoconductivity, low-temperature conductivity, and magnetoresistance studies on the layered semiconductor GaTe, Phys. Rev. B 63, 235321 (2001).
- [38] S. Anissimova, S. V. Kravchenko, A. Punnoose, A. M. Finkel'stein, and T. M. Klapwijk, Flow diagram of the metalinsulator transition in two dimensions, Nat. Phys. 3, 707 (2007).
- [39] L. M. Corliss, N. Elliott, and J. M. Hastings, Antiferromagnetic structure of CrN, Phys. Rev. 117, 929 (1960).
- [40] P. A. Bhobe *et al.*, Evidence for a correlated insulator to antiferromagnetic metal transition in CrN, Phys. Rev. Lett. **104**, 236404 (2010).
- [41] J. D. Browne, P. R. Liddell, R. Street, and T. Mills, An investigation of the antiferromagnetic transition of CrN, Phys. Status Solidi 1, 715 (1970).
- [42] F. Rivadulla *et al.*, Reduction of the bulk modulus at high pressure in CrN, Nat. Mater. **8**, 947 (2009).
- [43] K. Alam *et al.*, Structural and magnetic phase transitions in chromium nitride thin films grown by Rf nitrogen plasma molecular beam epitaxy, Phys. Rev. B 96, 104433 (2017).
- [44] A. Filippetti, W. E. Pickett, and B. M. Klein, Competition between magnetic and structural transitions in CrN, Phys. Rev. B 59, 7043 (1999).
- [45] A. Filippetti and N. A. Hill, Magnetic stress as a driving force of structural distortions: The case of CrN, Phys. Rev. Lett. 85, 5166 (2000).
- [46] B. Biswas, S. Chakraborty, O. Chowdhury, D. Rao, A. I. K. Pillai, V. Bhatia, M. Garbrecht, J. P. Feser, and B. Saha, In-plane Cr₂N-CrN metal-semiconductor heterostructure with improved thermoelectric properties, Phys. Rev. Mater. 5, 114605 (2021).
- [47] B. Biswas, S. Chakraborty, A. Joseph, S. Acharya, A. I. K. Pillai, C. Narayana, V. Bhatia, M. Garbrecht, and B. Saha, Secondary phase limited metal-insulator phase transition in chromium nitride thin films, Acta Mater. 227, 117737 (2022).
- [48] K. Liu, S. Lee, S. Yang, O. Delaire, and J. Wu, Recent progresses on physics and applications of vanadium dioxide, Mater. Today 21, 875 (2018).
- [49] R. Scherwitzl, P. Zubko, I. G. Lezama, S. Ono, A. F. Morpurgo, G. Catalan, and J.-M. Triscone, Electric-field control of the metal-insulator transition in ultrathin NdNiO₃ films, Adv. Mater. 22, 5517 (2010).
- [50] B. Biswas *et al.*, Magnetic stress-driven metal-insulator transition in strongly correlated antiferromagnetic CrN, Phys. Rev. Lett. **131**, 126302 (2023).
- [51] A. le Febvrier, D. Gambino, F. Giovannelli, B. Bakhit, S. Hurand, G. Abadias, B. Alling, and P. Eklund, p-type behavior of CrN thin films via control of point defects, Phys. Rev. B 105, 104108 (2022).
- [52] T. Rojas and S. E. Ulloa, Energetics and electronic structure of native point defects in antiferromagnetic CrN, Phys. Rev. B 98, 214111 (2018).
- [53] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.111.085302 for methods and electronic and structural characterization of the CrN films.
- [54] M. E. McGahay, S. V. Khare, and D. Gall, Metal-insulator transitions in epitaxial rocksalt-structure Cr_{1-x/2}N_{1-x}O_x(001), Phys. Rev. B **102**, 235102 (2020).
- [55] D. Rao, A. I. K. Pillai, M. Garbrecht, and B. Saha, Scandium nitride as a gateway III-nitride semiconductor for both excitatory and inhibitory optoelectronic artificial synaptic devices, Adv. Electron. Mater. 9, 2200975 (2023).

- [56] P.-C. Wei, S. Chattopadhyay, M.-D. Yang, S.-C. Tong, J.-L. Shen, C.-Y. Lu, H.-C. Shih, L.-C. Chen, and K.-H. Chen, Roomtemperature negative photoconductivity in degenerate inn thin films with a supergap excitation, Phys. Rev. B 81, 045306 (2010).
- [57] R. Wang, J.-L. Wang, T. Liu, Z. He, H. Wang, J.-W. Liu, and S.-H. Yu, Controllable inverse photoconductance in semiconducting nanowire films, Adv. Mater. 34, 2204698 (2022).
- [58] N. K. Tailor, C. A. Aranda, M. Saliba, and S. Satapathi, Negative photoconductivity: Bizarre physics in semiconductors, ACS Mater. Lett. 4, 2298 (2022).
- [59] T. Cheiwchanchamnangij and W. R. L. Lambrecht, Quasiparticle self-consistent GW-band structure of CrN, Phys. Rev. B 101, 085103 (2020).
- [60] S. Rudra, D. Rao, S. Ponce, and B. Saha, Dominant scattering mechanisms in limiting the electron mobility of scandium nitride, Nano Lett. 24, 11529 (2024).