REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
16-11-2015	Final Report	15-Aug-2014 - 14-Aug-2015

4. TITLE AND SUBTITLE
Final Report: Tunable high pulse energy ultrafast laser system

5a. CONTRACT NUMBER
W911NF-14-1-0465

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611103

6. AUTHORS
Norman Tolk

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Vanderbilt University
1400 18th Avenue South

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
65208-MS-RIP.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
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The first research area covers coherent acoustic phonon (CAP) spectroscopy of 4H silicon carbide (SiC) crystals. We will expand our present work on SiC to examine how an ion implantation process modifies the acousto-optical structure. The emphasis of our research remains on phenomena and processes far from equilibrium.
In the second research project we intend to study transient and permanent material modification at a specified depth

15. SUBJECT TERMS
Coherent acoustic phonons, Ultra-fast laser, carrier and phonon dynamics, far from equilibrium

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Norman Tolk
UU	UU	UU	UU		19b. TELEPHONE NUMBER 615-322-2786

Report Title

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A Final Report to the Department of Defense

Army Research Office

For ARO (DURIP) award No. W911NF-14-1-0465

Submitted November 16, 2015

Tunable high pulse energy ultrafast laser

by

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Abstract

In this final report we discuss the acquisition and set up of the newly acquired high power ultrafast laser system and outline our research plans using the system.

The first research area covers coherent acoustic phonon (CAP) spectroscopy of 4H silicon carbide (SiC) crystals. We will expand our present work on SiC to examine how an ion implantation process modifies the acousto-optical structure. The emphasis of our research remains on phenomena and processes far from equilibrium.

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In the third area of our research, we plan to explore and develop low-temperature diamond growth process assisted by ultrafast, high-power laser pulses. Our preliminary results are very promising and show that the pretreatment of substrate with ultrafast laser radiation improves the diamond growth significantly.

a) Technical parameters of the high power laser system

This DURIP award was used to acquire a Spectra-Physics ultrafast laser system (Figure 1) that includes a Ti:Sapphire oscillator with a cw pumping laser (MaiTai) and a 45 W pulsed Nd:YLF laser (Empower) to pump a regenerative amplifier (Spitfire Ace) with 6.5 W output power and a variable repetition rate (from 1 Hz to 10 kHz with a step of 1 Hz). The system which was installed December, 2014. This system is state-of-the art among high-energy ultrafast systems with pulse duration (bandwidth) of 100 fs (12 nm). The Spitfire Ace-PA-401K provides low noise, long-term power and temperature stability, day-to-day reproducibility. It is fully compatible with our existing two Optical Parametric Amplifiers (Quantronix/ Light Conversion TOPAS). The stable spectral range achievable extends from ~ 200 nm to > 20 μm (roughly 6.0 eV – 0.06 eV). The system is designed so that such wavelength selection is operationally readily facilitated.

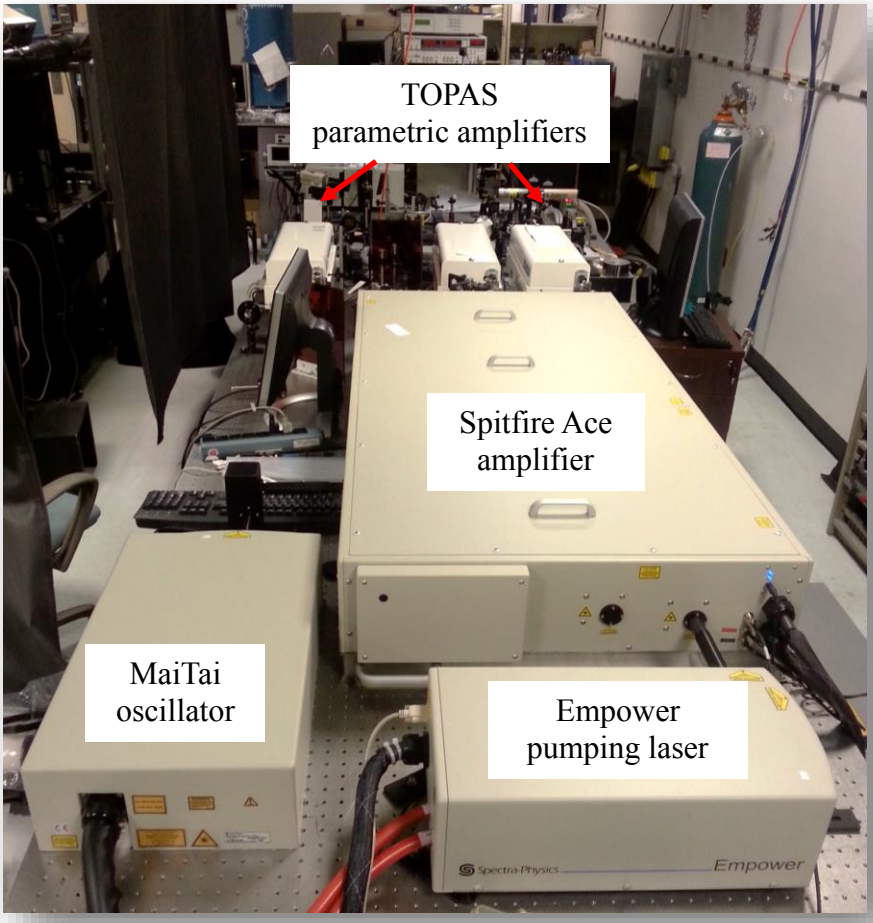

Figure 1. High-power ultrafast laser system.

To upgrade and enhance the apparatus, two existing optical parametric amplifiers (TOPAS) were adapted and joined to the new laser system (Figure 2). A telescope to limit the

diameter of the beam originating from the amplifier was constructed (Figure 2). Subsequently, a new pump-probe reflection and coherent acoustic spectroscopy system was put in operation (Figure 3). These system improvements were carried out from January, when the new laser was delivered to the beginning of March, 2015. During followed 8 months (mid-March through mid-November) the laboratory was not operational due to a mishap. In March, 2015 a flood occurred and after this accident the lab space had to be renovated and rearranged. Following this, the laser system was realigned and inspected by Spectra-Physics, the company from which the new laser system was purchased, and found to be working within specs.

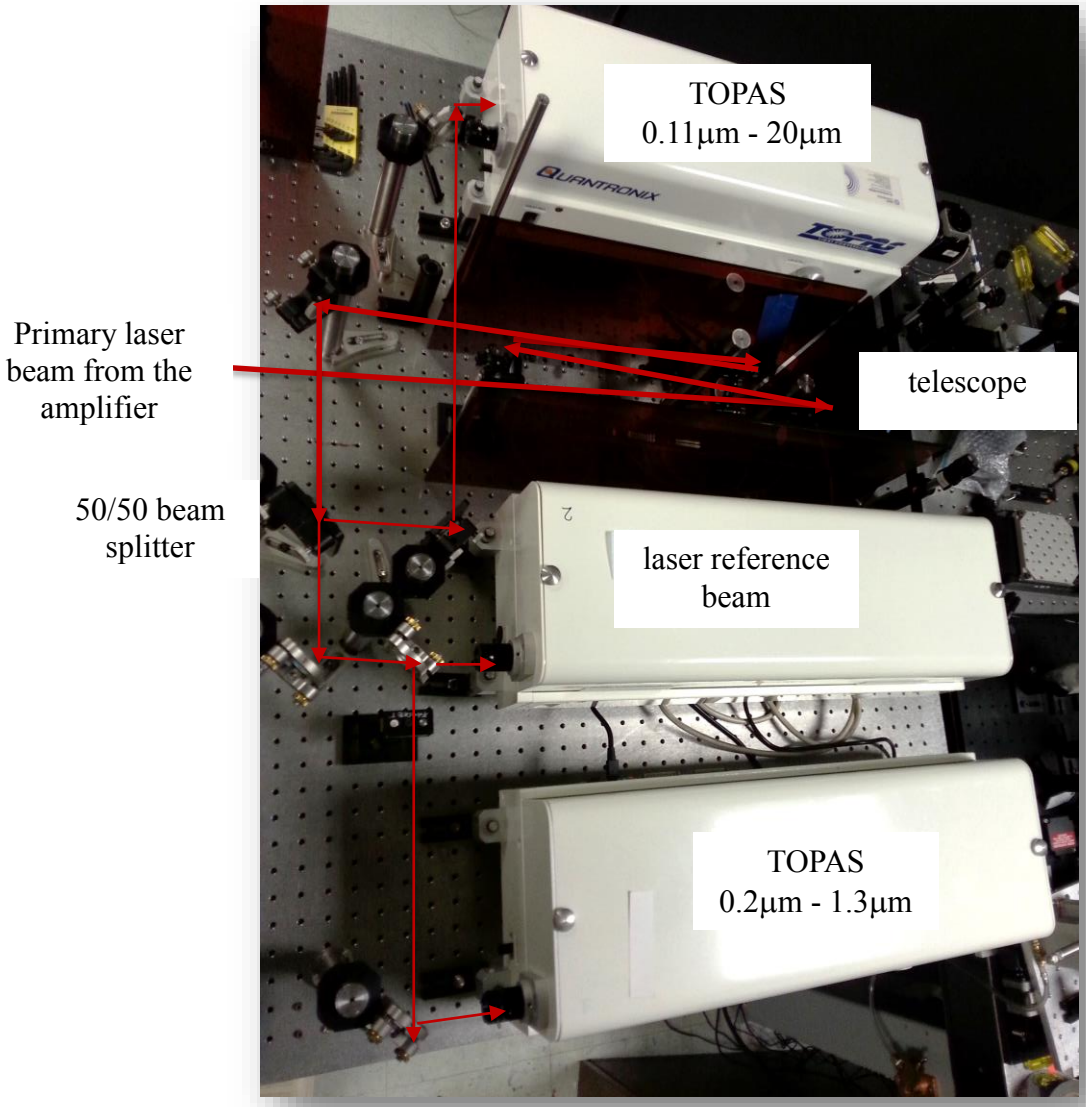

Figure 2. Two tunable parametric amplifiers with a telescope and a delay stage with the reference laser beam (top view).

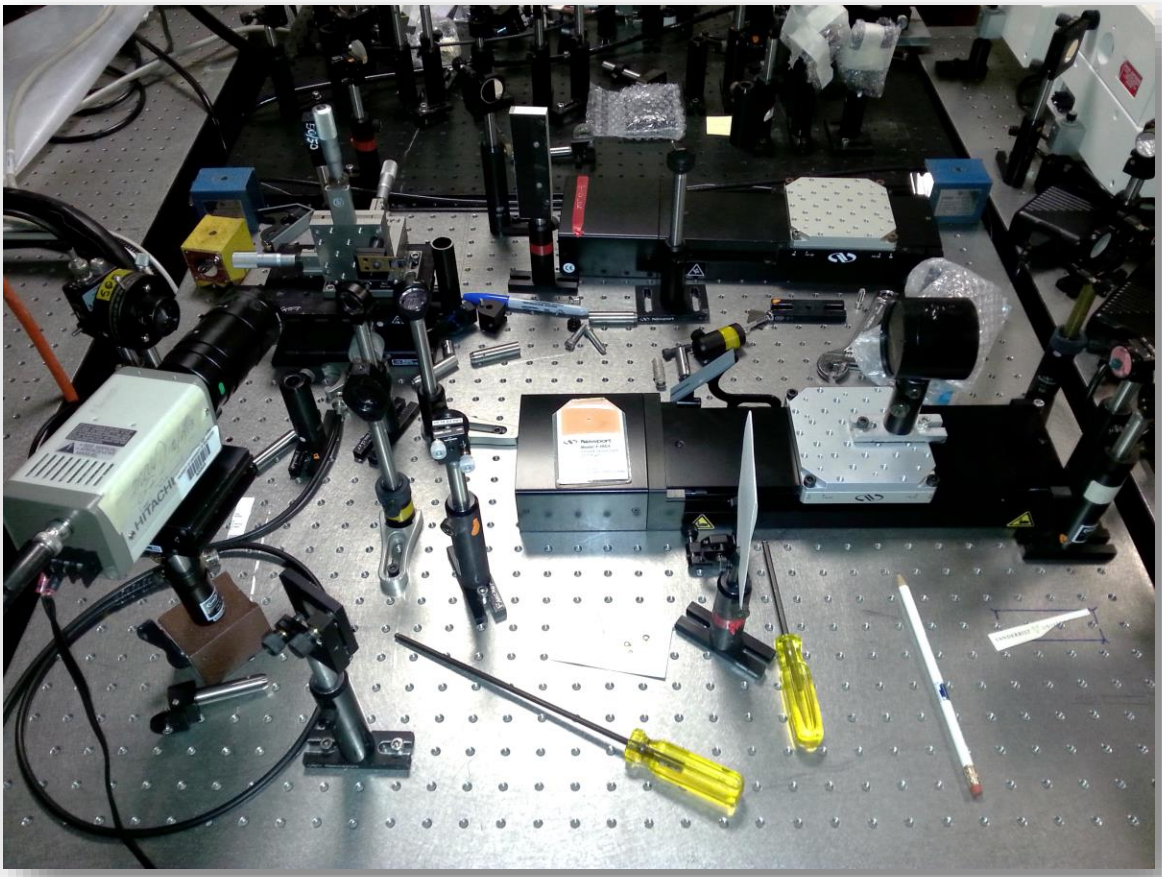

Figure 3. New built pump-probe reflection and coherent acoustic spectroscopy system.

b) Present measurements

Recently, we began testing the completed optical system (the laser system with two TOPAS and CAP spectrometer). Preliminary measurements on a single crystal silicon carbide (SiC) are shown in Figure 4. The CAP oscillations agree very well with our previous experiments. The pump wavelength was 800 nm and the probe was set as 400 nm. Various power of the pump beam was applied.

Fitting experimental data for the unimplanted SiC sample with equation (1) gives us $T =$ and $\tau =$. Using these fitted parameters, we calculate n and κ from formulae (3) and (4) with $v_s = 13.1$ nm/ps and $\lambda = 400$ nm to be $n = 3.11$ and $\kappa = 0.011$. These values are in good agreement with previously reported [1]

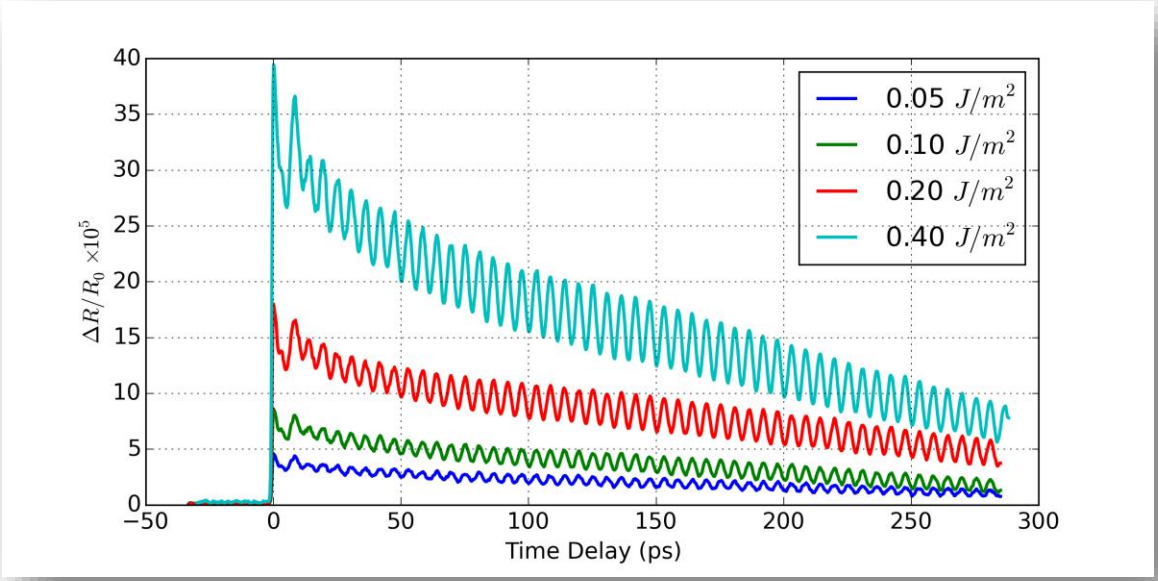

Fig. 4. Isolated oscillatory CAP responses for crystalline SiC specimen exposed to various pump power density per laser pulse.

c) Progress on research projects

1) H^+ implanted SiC and determination of optical constants

We plan to study ion beam-induced optoelectronic modifications in SiC as a function of depth and implantation dose using CAP spectroscopy. The basic effect is well explained by defect-modified changes in the electronic properties near the semiconducting band edge. A simple geometric model of the dose dependence suggests that band-gap renormalization may be characterized by a defect induced strain field that modifying the electronic structure at hundreds of nearby lattice points. While this effect is quite long-range for energies very near the band edge it reduces dramatically as the energy is detuned from E_g. Our results will show optical modification surrounding the amorphous state extends well beyond the structural disorder, suggesting a fundamental upper limit for the achievable density of bits/cm^2 in optical applications. These examples serve to highlight the importance of the relationship between structural and optoelectronic disorder in a wide variety of applications.

In this project, we will utilized coherent acoustic phonon waves to measure continuously varying defect concentrations in SiC crystals as a function of depth, using near-band-gap photon energies to maximize the sensitivity to small perturbations in local optical properties caused by defects. Defect concentrations in SiC specimens created through H^+ ion implantation over a wide range of doses ($1x10^{14}$ cm^{-2} – $1x10^{16}$ cm^{-2}), reliably creating

damage profiles consisting of vacancy and interstitial defects, which can be simulated using the transport of ions in matter (TRIM) code. The detailed analysis will provide depth profiles of optical constants.

The oscillatory part of the reflectivity response measured in CAP spectroscopy can be characterized as [2][3]

$$\frac{\Delta R(t)}{R_0} \propto A \sin\left(\frac{2\pi t}{T} + \phi\right) e^{-\frac{t}{\tau}}, \tag{1}$$

where t is time, T is period, τ is damping time, and ϕ is phase. As CAP wave travels with speed of sound time t is related to the depth z in the material by $z = v_s t$. Oscillation amplitude A is proportional to differential of complex refractive index N with respect to strain η caused by CAP wave

$$A \propto \left|\frac{\partial N}{\partial \eta}\right| \tag{2}$$

Period of oscillations T depends on real part of refractive index n, speed of sound (CAP wave) v_s, wavelength λ and angle of incidence θ of the probe beam as

$$T = \frac{\lambda}{2 n v_s \cos\theta}. \tag{3}$$

Damping time τ is proportional to penetration depth of the probe beam and, consequently, extinction coefficient κ

$$\tau = \frac{\lambda}{4\pi\kappa v_s}. \tag{4}$$

As it can be seen from equations (1-4) above CAP oscillatory response primarily depends on $n, \kappa, \partial n/\partial\eta, \partial\kappa/\partial\eta$. In case of ideal single crystals these values are constants with respects to depth. However, after ion implantation induced lattice damage make them depth dependent. The reduction in oscillatory amplitudes caused by radiation damage in SiC lattice can be attributed to (a) modification of the extinction coefficient induced by lattice defects or (b) changes of the refractive index.

As doses of implantation increases amplitude of oscillation decreases and phase shift induced (not seen easily). Such changes are related to change in complex refractive index. Thomsen theory tells us that cap response depend on $n, k, dn/d\eta, dk/d\eta$. We attribute changes in amplitude to changes in extinction coefficient and phase shift to changes in refractive index.

$$\frac{d\tilde{N}}{d\eta} = \frac{d\tilde{N}}{dE}\frac{dE}{d\eta}$$

We assume dN/dE to be constant. Than we can attribute amplitude attenuation change to extinction coefficient variations due hydrogen irradiation. This can be explained by the formula:

$$\frac{A}{A'} = \frac{4\pi}{\lambda}\int_0^z \Delta k(z')dz'$$

Phase shift is related to the real part of the refractive index and the speed of sound:

$$\Theta = \frac{2\pi n_0}{\lambda}\left[\int_0^z n(z')dz' - n_0 z\right]$$

2) Ultrafast dynamics of depth-dependent transient and permanent materials modification utilizing laser induced band gap narrowing

The major scientific objective of the research proposed here is to experimentally demonstrate and subsequently characterize ultrafast laser induced spatially localized transient states and ultimately permanent states in the materials of interest. Implementing this program requires utilizing the concept of transient modification (narrowing/broadening) of the band gap in host materials by ultrafast laser-induced transient strain (CAP), followed by intense ultrafast photo-excitation pulses at appropriate wavelengths to locally, at a specific depth, excite carriers in the material.

This proposal covers the following experimental works: (1) demonstration and characterization of localized electronic excitations at an arbitrary depth, utilizing coherent acoustic phonon (CAP) spectroscopy, (2) basic studies of i): energy flow and relaxation dynamics of transient, highly localized, excited carriers at a given depth; ii) effects of defects, impurities and strain using ultrafast pump-probe techniques; iii) as well as studies of dynamical processes leading to permanent modification, and (3) *in situ* characterization of permanently modified regions by pump-probe techniques, CAP spectroscopy and other materials probes. GaAs and Ge have been chosen initially as representative materials since both exhibit significant realizable change in the energy band gap arising from CAP induced transient strain.

A thin layer of metal (Al or Au) will be used as a transducing layer to generate coherent acoustic phonons. Then, using a regenerative amplifier for the optical pump in combination with a tunable optical parametric amplifier for the excitation pulses, thin layers within the specimens will be activated (i.e. electron excitation within the thin layer) over varying exposure times and excitation fluences. *In situ* characterization of the activation process will be accomplished by adding an additional probe pulse as described below. Using the standard CAP approach, the appropriate time delay for the desired modified layer depth will be determined.

The following experimental goals are identified:

- Given the localized electronic excitations at an arbitrary depth as described above, detect its presence and confirm its actual depth using CAP spectroscopy.
- For these depth dependent localized excitations, use ultrafast pump-probe approaches to assess carrier decay rates, often determined by carrier-phonon

interactions in the modified solid, leading to a basic understanding of the relaxation dynamics energy flow processes in the examined systems.

- Introduce defects, stress and impurities into the system to experimentally determine how this affects the measured relaxation dynamics.
- Identify a system amenable to permanent modification, use pump-probe experiments to determine carrier and phonon decay rates leading to the permanent modification.
- Finally, use the CAP technique and other materials probes such as TEM, to characterize the permanently modified materials at a specific depth.

At present, we anticipate the following list of possible material systems in which we could realize the creation of permanent highly localized material and band-gap modification:

1. Non-thermal dopant activation in, for example, implanted GaAs/depth selective *recrystallization* within the damage profile of implanted hosts;
2. Modulation doping, for example, doping of a heterostructure of materials with almost identical lattice constants but different band gaps (e.g. AlGaAs/GaAs).
3. Stimulation of electron migration in MBE fabricated delta-layers;
4. Smart cut – creation of near-monolayer damage regime(s) which lend themselves to subsequent selective etching with concurrent, spatially precise, intended material separation;

Memory materials - highly depth selective and extremely thin internal layer(s) where a phase change, e.g., conductive to dielectric or vice versa, has been induced with the non-thermal, tightly controlled interaction of ultrafast photons with coherent acoustic phonons.

Based upon our knowledge from previous phases, we will be in a position to decide upon a particular system to make permanent modifications. As a plausible example to proof the permanent modification idea, we have chosen to examine non-thermal dopant activation

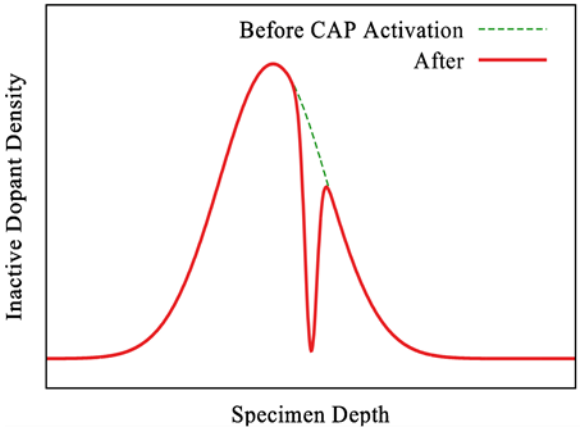

Fig. 5. Schematic concentration profiles for electronically inactive dopant impurities before and after localized activation using CAP strain waves

in implanted GaAs/depth selective *recrystallization* within the damage profile of implanted hosts.

Owing to our approach discussed in the previous sections, we will be able to deposit energy locally in non-thermal manner and to activate implanted dopants in thin layers with precisely selected depths. The depth will be defined by varying the time delay between the pump and activation pulses. The cartoon of profile of implanted ions in a host is placed in Figure 5. We will focus on GaAs and Ge samples implanted with Si and P.

We have assumed throughout this paragraph that damage created during implantation does not affect energy band gap significantly. Recent studies show that, for example, GaAs remains crystalline below 10^{14} cm^{-2} implantation dose of Si ions at room temperature due to self-annealing.

3) Low-temperature film growth - room-temperature deposition processes assisted by ultrafast laser pulse

The numerous material advantages of diamond have enticed many researchers to examine it as a potential alternative to silicon in the semiconductor industry. The major obstacle preventing the widespread use of diamond is the unconventional and often unreliable fabrication methods. Further, a technique to mass-produce diamond wafers, such as the Czochralski method for silicon, has not yet been developed. Our novel approach to diamond deposition utilizing ultrafast laser techniques has the prospect of overcoming many of these hurdles.

One significant advantage of our technique eliminates the need to pretreat the substrate prior to deposition. Most commonly, the heteroepitaxial deposition of diamond requires abrading the substrate surface as diamond growth occurs most favorable at defect sites. Further pretreatment typically involves nucleating the surface with nanodiamond structures to expedite the deposition time. We have found that stimulating the substrate surface through high-power ultrafast excitations can be substituted for these pretreatment steps yet only at predefined locations on the substrate. Thus, we have developed the first known method for the selective heteroepitaxial deposition of diamond, potentially paving the way for an all-diamond integrated circuit. Unfortunately, the inadequacies of our current system (too low output power) have limited us to deposition areas of only 1-2 mm in diameter. The new system we are requesting will further extend our current approach to permit deposition on large, commercially available substrates (1-2" in diameter).

Chemical vapor deposition (CVD) is a critical state-of-the-art process for the fabrication of thin films and coatings on arbitrary substrates. However, conventional deposition recipes require elevated substrate temperatures (>800 °C) to supply surface reaction energy, which excludes many desirable but fragile substrates from CVD processes. We have recently demonstrated enhanced low-temperature (300–400 °C) hot filament CVD diamond film deposition on silicon and diamond substrates using ultrafast laser excitation. The requisite surface reaction energy is supplied *non-thermally* by energetic photo-excited electrons, which create reactive sites by desorbing H directly and by the vibrational excitation of the C-H bond thus facilitating H abstraction. This non-equilibrium process results in negligible substrate heating due to the low duty cycle of the pulsed laser. Enhanced film quality and growth rate have been verified using secondary electron microscopy and Raman spectroscopy. We propose to build on these exciting preliminary

results through further exploration of the effects of laser power, wavelength, and growth conditions on deposition rates and film quality, with ultimate the goal of achieving near room-temperature film growth.

Summary

We are pleased to report that the new laser system financed by a DURIP grant has been acquired, configured and just now put into operation. With regard to cutting edge research thrusts enabled by the newly acquired laser system, we intend to initiate experimental work related to three research areas. The first is coherent acoustic phonon (CAP) spectroscopy of silicon carbide crystals. In preliminary measurements we have shown that the ion implantation process significantly modifies the acousto-optical structure of silicon carbide, resulting in a variety of significant features in the observed CAP spectra. These features were examined as a function of implantation dose and an empirical model was applied to the data, yielding good agreement. We have used this data to determine depth-dependent profiles of optical constants in the implanted samples.

We intend in the second research project to study transient and permanent material modification at a specified depth in semiconductors caused by a spike of localized, high density excited carriers due to coupling between photons and coherent acoustic phonons. These studies are based on the recognition that the semiconductor band gap is transiently narrowed by the CAP wave allowing localized electronic excitation at a desired depth by properly timed laser pulses of appropriate energies.

Finally, we plan to explore and develop low-temperature diamond growth process assisted by ultrafast, high-power laser pulses. Our preliminary results are very promising and show that the pretreatment of substrate with ultrafast laser radiation substantially improves the rate and quality of diamond growth.

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