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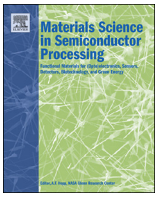

Octahydroacridine thin films grown by matrix-assisted pulsed laser evaporation for non linear optical applications

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ABSTRACT

We report on the thin film growth of *1,2,3,4,5,6,7,8-octahydroacridine* (OHA) by matrix-assisted pulsed laser evaporation (MAPLE), starting from a frozen solution of 1% OHA dissolved in methanol and using a Nd:YAG laser emitting at 266 nm wavelength with fluences in the range 0.1–1 J/cm^2. The optical properties were studied by spectroscopic-ellipsometry (SE), while Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), and scanning electron microscopy (SEM) were performed for structure and surface morphology investigation. Second harmonic generation (SHG) capabilities of the thin films were investigated by using a tunable Ti:sapphire laser with maximum emission centred in near infra-red. The peak of emitted photons is located at 388 nm, therefore half the wavelength of the initial photons (776 nm). The semi logarithmic dependence of SHG intensity on incident power is almost linear, except the value obtained at highest power of incident photons. This value indicates a local changing of sample due to the heating produced by the high-power incident beam.

1. Introduction

Acridine ($C_{13}H_9N$) is a stable, weakly basic compound, structurally related to anthracene ($C_{14}H_{10}$) with one of the central CH groups replaced by nitrogen [1,2]. Pure acridine was first isolated in 1871 by Carl Gräbe and Heinrich Caro, as it naturally occurs in coal tar. Its derivatives are a class of materials with a large area of applications, most of them known human carcinogens, causing frameshift mutations by incorporating into the DNA and creating an additional base on the opposite strand [1–5]. They have been widely used as antibacterial and antiprotozoal agents, *e.g.* the acridone derivatives, synthesized by the *Lehmstedt-Tanasescu* reaction [6,7], or other type of drugs [1,3–5]. In the last few years, the acridine-based compounds drew attention upon their non-linear optical properties [8–10]. One such compound is *1,2,3,4,5,6,7,8-octahydroacridine* ($C_{13}H_{17}N$) or OHA, a white crystalline solid that is less toxic compared to acridine [11,12]. OHA and its derivatives are of great interest as they play an important role in the preparation of agrichemicals, alkaloids, dyes, medicines, drugs and other biologically active compounds with intriguing pharmacological and therapeutic properties in cancer and Alzheimer's disease treatments, and advanced functional materials precursors [1,2,13,14]. Today, OHA can be easily synthesized by different routes [14–30], making it an economically attractive candidate for various

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applications due to its excellent price/quality ratio. Among these applications, non-linear optical (NLO) properties that may arise from particularities of the OHA molecule (*i.e.* influence of conformational asymmetry due to the tricyclic structure) make it suitable for bulk and thin film second harmonic generation (SHG) investigations [30,31].

Here, we report on the deposition of OHA thin films by matrix-assisted pulsed laser evaporation (MAPLE), starting from a frozen solution of 1% OHA dissolved in methanol. The optical properties of the films were studied by spectroscopic-ellipsometry (SE). Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), and scanning electron microscopy (SEM) were employed for structure and surface morphology investigation. SHG capabilities of OHA thin films were evidenced by using a femtosecond pulsed laser.

2. Experimental

Direct laser irradiation, *e.g.* by pulsed laser deposition (PLD) of organic molecules may induce photo-chemical decomposition and pyrolysis [32]. The MAPLE technique uses an absorbing matrix (i.e. the solvent, typically using concentrations of 1–4%) that acts like a protection for the molecules [32–34], although some interesting inverse effects have recently also been pointed out [35]. Furthermore, the MAPLE technique is also suitable in making multilayered thin films and/or embedded structures, when no compatible solvents are available for simpler techniques, such as spin coating, dropcasting, and dip-coating.

In our MAPLE experiments we used a 1% solution of laboratory synthesized OHA [24,30], carefully frozen in liquid nitrogen in a copper target holder [36–39]. The target holder was kept solid throughout thin film growth procedures. From our previous experience and based on literature studies [34–40], the laser fluence was chosen in the range of 0.1–1 J/cm^2 (Nd:YAG, "Surelite II" pulsed laser system from Continuum Company: 266 nm wavelength, 7 ns duration of the pulse, 10 Hz), using a 2 mm^2 spot. All depositions took place in vacuum (1×10^{-4} mbar), with the chamber being continuously pumped by a "Pfeiffer-Balzers 4 TPU 170" turbomolecular system (170 l s^{-1} volume flow rate). The target was irradiated with 40000 laser pulses, in order to evidence thin film thickness dependence to its morphology and optical properties. The substrates, i.e. polished Si wafer (on both sides), and indium tin oxide (ITO) covered BK7 glass slides, were kept at room temperature during thin film growth. Prior to the deposition, the substrates were cleaned by ultrasonic bath for 15 min, using acetone and isopropanol as cleaning mediums, and then dried in nitrogen gas flow. The target—substrate distance was chosen to be 3.5 cm, with the target rotated during MAPLE.

Thin film morphology and surface roughness were analyzed by atomic force microscopy (AFM) using a "XE-100" setup produced by Park Systems. These investigations were made in non-contact mode using a silicon carbide tip (10 nm radius of curvature). Fourier transform infrared absorption spectra of the OHA thin films grown by MAPLE on double side polished Si wafers were compared to the dropcast films. The measurements have been performed using a Jasco 6300 FTIR machine, in the range 400–4000 cm^{-1} (resolution: 4 cm^{-1}). Optical measurements were performed by using a Woolam Vertical Variable Angle Spectroscopic Ellipsometer (V-VASE), equipped with a high-pressure Xe discharge lamp incorporated in an HS-190 monochromator. Spectroscopic-ellipsometry measurements were performed between 400 and 1000 nm spectral range (step of 2 nm), and fixed angle of incidence (60°). The investigations of SHG capabilities were made using a setup that includes: a tunable Ti:sapphire laser with maximum emission centred at 800 nm (Spectra Physics, 60–100 fs pulse duration, 80 MHz repetition rate, 700 mW output power); an optical system that allows the variation of beam intensity (made using a half-wave plate and a *Glan–Taylor* polarizing prism, that allows to reach continuous range of 0–400 mW); and a microscope objective (20 ×) that focalizes the laser beam onto the OHA thin film samples. The intensity of the emitted SHG radiation is collected through fiber-optic cables and measured by an iCCD camera spectrograph from ANDOR.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy

FTIR absorption measurements have been performed on the starting material, as a dropcast thin film, in order to get the corresponding OHA fingerprint. The results were compared to those originating from thin films deposited by MAPLE, in order to identify the best deposition conditions.

In Fig. 1, two spectra are presented, corresponding to the starting material (dropcasted), and to the MAPLE grown thin film, grown at 0.3 J/cm^2. One can immediately notice the resemblance between the OHA dropcasted film vs. the MAPLE one, pointing out its structural preservation upon laser processing. The OHA-related vibrations can be grouped as follows: vibrations originating from the pyridine ring and vibrations due to aliphatic cycle, respectively [13,14]. The spectrum consists in the acridine characteristic vibrations, combined with the vibrations of the simple bonds from the aliphatic group [41,42]. Specifically, the peaks observed at approximately 1520 cm^{-1} and 1599 cm^{-1} are related to the ring stretching vibration of the pyridine compound. The bands positioned at 2911 cm^{-1} and 2839 cm^{-1} are related to the

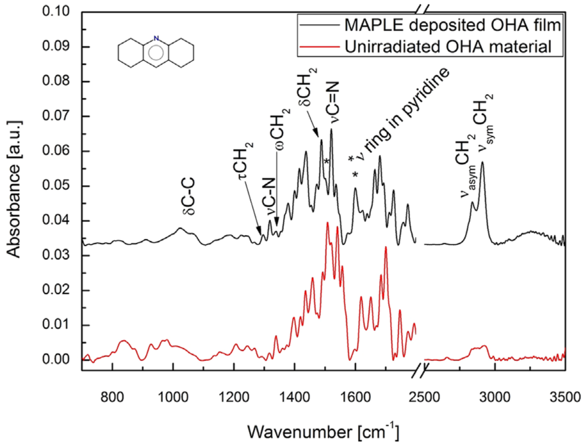

Fig. 1. FTIR absorption spectra of dropcast vs. MAPLE grown OHA thin films (0.3 J/cm^2 laser fluence, 2 mm^2 laser spot area, 40 000 pulses), and the molecular structure of OHA (upper left side inserted image).